ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. VI. THE ACTION ON CYCLOHEXYLAMINE AND ITS DERIVATIVES.*

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Cyclohexylamine as well as chloro- and iodo-cyclohexanes, when heated with hydrogen iodide in a sealed tube at 200° for several hours, produces methylcyclopentane.(1) One of the authors has previously(2) observed that cyclohexanol and its derivatives are converted chiefly into methylcyclopentane and its derivatives respectively by the catalytic action of Japanese acid earth heated at 300° under ordinary pressure, while at 200° they are mainly converted into cyclohexene and its derivatives respectively.

The present experiments were undertaken to ascertain whether cyclohexylamine and its derivatives also undergo the same isomeric change from the six-membered carbon rings to the five-membered ones by the contact action of the acid earth.

The amines used in the experiments were prepared from the corresponding phenols; pure carbolic acid and three isomeric cresols were reduced to hexahydrophenols by Sabatier and Sendrens's method, which were then oxidized with chromic acid, and the resulting ketones were changed into their oximes, from which the required amines were obtained by the reduction with metallic sodium and absolute alcohol. At every stage of the preparation, care was especially taken for purification, all the specimens being therefore very pure and entirely free from aromatic amines. The catalyst, dried at 300°, filled a glass tube with a length of 1 metre and a diameter of 2 cm., and was heated to 350° electrically, and then the weighed amount of an amine was passed on it. The liquid reaction product was passed through a condenser and collected in a receiver and the escaping gaseous product was bubbled into a series of washing bottles containing normal sulphuric acid to catch ammonia evolved.

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(1) Markonikoff, *Ber.*, **30** (1897), 1225; *Ann.*, **302** (1898), 36; ibid., **307** (1899), 336; Zelinsky, *Ber.* **30** (1897), 388. This work was carried out in 1927–1928. Recently Nenitzescu and Cantuniari (*Ber.*, **66** (1933), 1097) observed that cyclohexane is converted into methylcyclopentane when boiled with moist aluminium chloride.

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(2) Inoue, This Bulletin, **1** (1926), 219; ibid., **9** (1934), 353.

I. Cyclohexylamine. The amine (b.p. 134°, d_4^{25} 0.8644, n_D^{25} 1.45757), (26.0 g.), being passed on the earth heated at 350° at the rate of 4.7 g. per hour, yielded 15.5 g. of an oily substance and 3.5 g. of gaseous ammonia. The oil was washed with cold dilute hydrochloric acid to remove basic substances, and then with a dilute soda solution and water, dried over anhydrous sodium sulphate, and thus 13.2 g. of a mixture of hydrocarbons (d_{20}^{20} 0.8264) were obtained, which, subjected to fractional distillation seven times, gave the fractions shown in Table 1.

Table. 1.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	70–76°	1.5	0.7654	1.4233
2	76–77°	2.0	0.7709	1.4263
3	77–80°	0.4	0.7741	1.4294
4	80–85°	0.1	—	—
5	Residue	2.5	0.9213	1.5135

As shown by the physical constants given in the table, the first fraction consists mainly of methylcyclopentane, whose presence was confirmed by the formation of succinic and acetic acids on oxidation according to Aschan.[3] As the yield of the fourth fraction was too small to determine its physical constants, the same experiment was repeated and the fraction with the boiling point 82–85° was collected, which was found to be almost pure cyclohexene by its physical constants (b.p. 82–85°, d_4^{20} 0.8046, n_D^{20} 1.44466).

The second and third fractions are mixtures of methylcyclopentane and cyclohexene, and the residue is a mixture of higher hydrocarbons, probably the polymers, condensed products, or both, of the above mentioned substances.

The basic substances were, as already stated, separated from the other reaction products by washing with dilute hydrochloric acid. The washing liquid was neutralized with caustic soda and extracted with ether. After the ether was driven off the free amines were weighed (Yield 0.4 g.). The amines were again dissolved in ether and left to stand. Some days after a white crystalline substance deposited on the wall of the vessel containing the ethereal solution, which was identified to be carbazole by its melting point (238°) and also by the characteristic colour reaction. Into the remaining ethereal solution dry carbon dioxide was passed under cooling with ice and common salt, thereby some unchanged cyclohexylamine was thrown down as carbonate. The solution separated from the insoluble carbonate was treated with benzoyl chloride and alkali. The benzoyl derivative pro-

(3) *Ber.*, **31** (1898), 1804.

duced was recrystallized from dilute alcohol and was found to be benzanilide (m.p. 159–160°). The presence of aniline in the basic reaction product was further confirmed by the colour reactions with bleaching powder and with potassium bichromate.

From the above results it may be concluded that ammonia is first split off from cyclohexylamine, cyclohexene being yielded just in the same manner as water is split off from cyclohexanol, and then the resulting cyclohexene undergoes the isomerization from the six-membered carbon ring to the five-membered one producing methylcyclopentane, some polymerization or condensation products being formed simultaneously. The dehydrogenating property of Japanese acid earth is also noticed in the fact that carbazole and aniline are produced.

II. **1-Methylcyclohexylamine-(2).** By passing 66.7 g. of 1-methylcyclohexylamine-(2) (b.p. 148–150°, d_4^{14} 0.8639, n_D^{16} 1.45917) on the acid earth heated at 350° at the rate of 3.3 g. per hour, 41.0 g. of an oily substance and 7.8 g. of gaseous ammonia were obtained. From the former 1.0 g. of basic substances was separated in the same manner as in the former experiment and 35.0 g. of a neutral oil (d_{20}^{20} 0.8066) was obtained, which was fractionated into nine parts after the seventh fractional distillation (Table 2). The parts boiling below 100° were again fractionated three times (Table 3).

Table 2.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 85°	4.2	0.7586	1.4201
2	85—90°	2.0	0.7716	1.4263
3	90—95°	2.5	0.7748	1.4282
4	95—100°	4.9	0.7763	1.4296
5	100—102°	3.8	0.7794	1.4325
6	102—104°	3.1	0.7841	1.4351
7	104—108°	3.9	0.7893	1.4388
8	108—112°	0.7	0.7961	1.4435
9	Residue	7.4	0.9133	—

Table 3.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	70—75°	1.0	0.7492	1.4144
2	75—80°	1.5	0.7630	1.4216
3	80—85°	1.3	0.7686	1.4245
4	85—90°	1.3	0.7727	1.4266
5	90—95°	2.4	0.7750	1.4282
6	95—100°	2.	0.7776	1.4298
7	Residue	0.7	—	—

The physical constants and the result of elementary analysis of the eighth fraction of Table 2 and the melting point (92–93°) of the nitrosochloride prepared from it by Faworsky and Bergmann's method,[4] well

(4) *Ber.*, **40** (1907), 4863.

accord with those of Δ^1-methylcyclohexene. (Found : C, 87.16 ; H, 13.02. Calc. for C_7H_{12} : C, 87.50 ; H, 12.50%.)

From the physical constants it may be safely stated that the fractions boiling between 102° and 108° consist mainly of Δ^2- and Δ^3-methylcyclohexenes. A greater yield of the liquid nitrosochloride of bluish green colour is obtained from the lower boiling fraction than from the higher boiling, which shows that the lower boiling parts are richer in Δ^3-methylcyclohexene, for, according to Markonikoff,[5] the nitrosochloride of Δ^3-methylcyclohexene is a bluish green liquid. (The nitrosochloride of Δ^2-methylcyclohexene is not yet found in literature.)

The fifth fraction of Table 2 (b.p. 100–102°), united with the corresponding fraction in another experiment carried out under the same conditions, was treated with concentrated sulphuric acid to remove unsaturated hydrocarbons, and 5.0 g. of the resulting saturated hydrocarbons was fractionated five times over metallic sodium (Table 4).

The physical constants of the first fraction of Table 4 indicate that it is almost pure ethylcyclopentane.

The fifth and sixth fractions of Table 3 (b.p. 90–100°) were combined together, treated with concentrated sulphuric acid, and fractionated again over metallic sodium (Table 5).

Table 4.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	90–98°	0.4	0.7632	1.4203
2	98–100°	1.6	0.7663	1.4221
3	Residue	0.7	0.8667	—

Table 5.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	90–96°	0.5	0.7591	1.4177
2	96–98°	1.1	0.7621	1.4195
3	98–100°	0.8	0.7646	1.4211
4	Residue	1.0	0.8625	—

The physical constants and results of elementary analysis of the first fraction of Table 5 (b.p. 90–96°) well accord with those of 1,2-dimethylcyclopentane. (Found : C, 85.49 ; H, 14.60. Calc. for C_7H_{14} : C, 85.71 ; H, 14.29%.) The second fraction (b.p. 96–98°) (Table 5) is ethylcyclopentane. (Found : C, 85.56 ; H, 14.47. Calc. for C_7H_{14} : C, 85.71 ; H, 14.29%.)

Ethylcyclopentane thus obtained may be contaminated with a small quantity of methylcyclohexane which is produced from methylcyclohexene by the contact action of concentrated sulphuric acid as one of the authors (H.I.) observed previously[6].

(5) *Bull. soc. chim.*, [3] **34** (1905), 219.
(6) This Bulletin, **1** (1926), 225.

The first fraction of Table 3 (b.p. 70–75°) is obviously methylcyclopentane. (Found: C, 85.92; H, 14.10. Calc. for C_6H_{12}: C, 85.71; H, 14.29%.)

In order to examine the presence of toluene in the reaction products, the fraction boiling between 108° and 112° (Table 2) was treated with concentrated nitric acid under cooling with ice and salt and then the resulting nitro-compound was reduced with tin and hydrochloric acid. The reduction product showed the colour reaction with β-naphthol, which is characteristic of aromatic amines. It was then converted into a benzoyl derivative and this was recrystallized from alcohol. Its melting point was 130°, identical with that of benzo-*o*-toluide. Toluene was therefore actually present.

Table 6.

Fraction	B.p. (2mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	40—60°	0.4	0.8707	1.4913
2	60—70°	0.5	0.8857	1.4966
3	70—80°	1.2	0.8969	1.5021
4	80—90°	1.6	0.9082	1.5101
5	90—95°	1.8	0.9200	1.5198
6	95—100°	0.5	0.9310	1.5296
7	100—105°	0.3	—	—
8	105—115°	0.2	—	—
9	115—125°	0.8	0.9557	1.5313
10	125—135°	1.6	0.9685	1.5700
11	Residue	1.2	—	—

It was thus possible to detect methylcyclpentane, ethylcyclopentane, dimethylcyclopentane, the three isomeric methylcyclohexenes, and toluene in the neutral reaction product. Methylcyclopentane may here be considered to have been formed not only from cyclohexene but also from ethylcyclopentane by the decomposition analogous to that of ethylcyclohexane into methylcyclohexane[7]. Other hydrocarbons are polymers boiling above 112°. The residue of Table 2 combined with those obtained by other experiments was distilled in steam. Thirteen grams distilled over out of 17.6 g., the distillate was then twice distilled under the pressure of 2 mm., and the fractions shown in Table 6 were obtained.

The largest portion of Table 6 is the fifth fraction boiling between 90° and 95°, which on analysis gave the following results[8]:

Found: C, 88.42; H, 10.96. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%.
Mol. wt. found: 174. Mol. wt. calc. for $C_{14}H_{20}$: 188.

The acid-soluble reaction product amounted to 1.0 g., from which *o*-toluidine was isolated as the benzoyl derivative, and unchanged methylcyclohexylamine as the carbonate.

(7) Sabatier and Sendrens, *Compt. rend.*, **132**, (1901), 856; ibid., **132**, 1255; *Ann. chim.*, [8] **4**, (1905), 365.

(8) The analysis was carried out after long standing of the sample, so a small amount of atmospheric oxygen seems to have been absorbed by it, some oxidation products being thereby formed.

III. 1-Methylcyclohexylamine-3. The amine (b.p. 149–151°, d_4^{20} 0.8472, n_D^{20} 1.45357) (68.5 g.) was passed on the acid earth heated at 350° at the rate of 2.7 g. per hour and 34.5 g. of a neutral oil (d_{20}^{20} 0.8053), 8.5 g. of gaseous ammonia, and 1.4 g. of a basic substance were obtained.

The neutral oil was submitted to fractional distillation seven times over metallic sodium and the fractions shown in Table 7 were obtained. The fractions boiling below 100° were further fractionated three times over metallic sodium (Table 8.) Compared with 1-methylcyclohexylamine-(2), 1-methylcyclohexylamine-(3) produces a much less quantity of the portion boiling below 90°, which in the latter case consists mainly of dimethylcyclopentane as shown by its physical constants and the result of elementary analysis (Found : C, 85.97 ; H, 14.10 . Calc. for C_7H_{14} : C, 85.71 ; H, 14.29%), but the presence of ethyl- and methyl-cyclopentanes was not definitely confirmed. The physical constants of the third fraction (b.p. 95–100°) of Table 7 are nearly equal to those of methylcyclohexane, which was not confirmed to be present in the reaction products of 1-methylcyclohexylamine-(2). The fractions boiling above 100° consist mainly of three isomeric methylcyclohexenes as in the former case. The nitrosochloride prepared from the

Table 7.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
	To 90°	0.3	—	—
2	90—95°	1.7	0.7617	1.4223
3	95—100°	4.7	0.7741	1.4294
4	100—102°	5.5	0.7808	1.4334
5	102—104°	6.9	0.7876	1.4377
6	104—108°	6.5	0.7942	1.4431
7	108—112°	1.2	0.8010	1.4485
8	Residue	5.7	0.9144	—

Table 8.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 90°	0.8	0.7552	1.4181
2	90—95°	0.9	0.7660	1.4233
3	Residue	4.1	0.7777	1.4295

Table 9.

Fraction	B.p. (5 mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	To 100°	0.4	0.8795	1.4992
2	100—115°	0.7	0.9251	1.5250
3	115—125°	0.4	0.9382	1.5359
4	125—135°	0.8	0.9632	1.5617
5	Residue	0.2	—	—

seventh fraction (b.p. 108–112°) melts at 92°, indicating the presence of Δ^1-methylcyclohexene, which was further confirmed by analysis. (Found : C, 87.01 ; H, 12.83. Calc. for C_7H_{12} : C, 87.50 ; H, 12.50%.) Toluene was again found in the same fraction, which was isolated as benzo-*o*-toluide. (Found : N, 6.48. Calc. for $C_{14}H_{13}ON$: N, 6.63%.) Its amount was,

however, much larger than in the case of 1-methylcyclohexylamine-(2). The residue of Table 7 was submitted to steam distillation, then distilled under the pressure of 5 mm. into the fractions given in Table 9.

In the basic reaction product a trace of *m*-toluidine was noticed together with some unchanged 1-methylcyclohexylamine-(3).

IV. 1-Methylcyclohexylamine-(4). The amine (b.p. 149–151°, d_4^{20} 0.8470, n_D^{20} 1.45157) (110.0 g.) was passed on the earth heated at 350° at the rate of 3.1 g. per hour, and 61.5 g. of a neutral oil (d_{20}^{20} 0.8049), 12.8 g. of gaseous ammonia, and 1.8 g. of a basic substance were obtained.

The neutral substance gave the fractions given in Table 10 after ten times fractional distillation over metallic sodium.

Table 10.

Fraction	B.p.	Yield (g.)	d_4^{25}	n_D^{25}
1	To 90°	0.2	—	—
2	90–95°	0.7	0.7531	1.4187
3	95–100°	2.3	0.7680	1.4253
4	100–102°	3.9	0.7754	1.4299
5	102–104°	10.9	0.7822	1.4335
	104–106°	12.2	0.7840	1.4376
7	106–108°	10.2	0.7948	1.4415
8	108–112°	3.8	0.7970	1.4444
9	Residue	8.0	0.8980	—

Table 11.

Fraction	B.p. (5 mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	To 97°	0.5	0.8776	1.4891
2	97–110°	1.2	0.9046	1.5046
3	110–115°	0.7	0.9129	1.5114
4	115–125°	0.8	0.9226	1.5198
5	125–135°	0.7	0.9450	1.5426
6	Residue	0.9	—	—

By the similar treatment of each fraction, three isomeric methylcyclohexenes, dimethylcyclopentane, and toluene were ascertained to occur. In this case, too, the presence of methyl- and ethyl-cyclopentanes was not confirmed.

The residue of Table 10 was distilled under the pressure of 5 mm. (Table 11). The fourth fraction of Table 11 (b.p. 125–135°) was analyzed.

Found: C, 89.38; H, 10.39. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%.
Mol. wt. found: 176. Mol. wt. calc. for $C_{14}H_{20}$: 188.

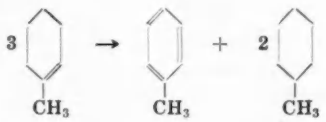
Here again a substance with a probable molecular formula of $C_{14}H_{20}$ was isolated, of which further study was not able to be done on account of the scantiness of the material. In the basic reaction product, *p*-toluidine, unchanged methylcyclohexylamine, and a small quantity of a white crystalline substance melting at 186–190°, probably a homologue of carbazole, were confirmed to occur.

Conclusion.

(1) One molecule of ammonia is first liberated from cyclohexylamine and its methyl derivatives when they are passed on Japanese acid earth heated at 350°, yielding cyclohexene and its methyl derivatives respectively. The molar yield of ammonia produced thereby corresponds to about 80 per cent. of the amine taken.

(2) Some part of cyclohexene thus produced then undergoes an isomeric change from the six-membered carbon ring to the five-membered one giving methylcyclopentane. Methylcyclohexenes suffer the similar isomerization giving ethyl- and dimethyl-cyclopentanes and some part of ethylcyclopentane is further decomposed to methylcyclopentane. The displacement of the double bond within the molecule of Δ^2- or Δ^3-methylcyclohexene must occur simultaneously giving Δ^1-methylcyclohexene, the most stable form of the three isomers, for, in the case of 1-methylcyclohexylamine-(4), Δ^1-methylcyclohexene can not be otherwise formed.

(3) The acid earth promotes also dehydrogenation, yielding aniline and carbazole from methylcyclohexylamine, and toluene from three isomeric methylcyclohexenes. Toluene is always accompanied by methylcyclohexane, and the yields of the two substances go parallel. The following mechanism may be therefore suggested, which Zelinsky[9] has proposed for the catalytic reaction of palladium.



The presence of benzene, however, was not confirmed in the reaction product of cyclohexylamine.

(4) Polymerization, condensation, or both, take place at the same time giving polymers or condensed products, whose amounts are about 15–20 per cent. of the total reaction product.

(5) The total quantity of cyclopentane derivatives is much larger in the case of cyclohexylamine than in the case of its methyl derivatives, while of the latter 1-methylcyclohexylamine-(2) gives the largest amount and 1-methylcyclohexylamine-(4) gives the least. It is also observed that the yield of polymers goes parallel to that of cyclopentane derivatives.

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(9) *Ber.*, **57** (1924), 2055.

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. VII. THE RELATION BETWEEN THE CONSTITUENTS OF THE EARTH AND ITS CATALYTIC ACTION.*

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It has been shown in the previous papers[1] that Japanese acid earth has various catalytic actions on various organic compounds. The earth is, however, not a definite compound and it seems most probable that it is essentially a kind of hydrated aluminium silicate mixed with colloidal silica[2] and small amounts of many other metallic oxides. Still it remains unknown which of these constituents plays a principal part in its characteristic actions except that it owes its oxidase-like actions to the minute quantity of manganese dioxide contained in it[3].

When a mixture of naphthalene and some dry powdered acid earth was heated at about 300° in a sealed tube, a marked amount of a resinous matter was produced, which was found mainly composed of β,β'-dinaphthyl. The rôles played by the chief constituents of the earth in this catalytic action were investigated in the present experiment.

The Resinous Matter. The reaction product in a sealed tube was extracted with benzene. After the benzene was distilled off the residue was distilled in steam to remove unchanged naphthalene, when a mass of chocolate colour was left behind in the distillation flask. About 70 per cent. of this resinous matter passed over between 260° and 310° under 28 mm., and solidified at once to a yellow crystalline mass. It was recrystallized several times from alcohol with the addition of animal charcoal. The colourless scales of β,β'-dinaphthyl were obtained, which melted at 182° when heated alone or with the authentic specimen synthesized from β-chloronaphthalene.

The earth after complete extraction with benzene has a grey colour and its weight increase is always 1–2 per cent. of the resinous matter produced,

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(1) Inoue, This Bulletin, **1** (1926), 157, 177, 197, 219; **9** (1934), 353; Inoue and Ishimura, ibid., **9** (1934), 423.

(2) Yamamoto, *J. Soc. Chem. Ind. Japan*, **34** (1931), 244 B; ibid., **36** (1933), 38 B, 460 B.

(3) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **33** (1930), 335 B; Iimori, *Bull. Inst. Phys. Chem. Research, Japan*, **9** (1930), 852.

and no other product is found. The yield of the resinous matter depends largely upon the temperature and the duration of the reaction as well as the amount and pre-treatment of the earth, yet it remains constant within about ±2 per cent. under a definite condition, and it can, therefore, be taken as a direct measure of the catalytic activity of Japanese acid earth on naphthalene.

The Standard Condition. The standard condition to measure the catalytic activity was chosen as follows: 25.00 g. of "pure naphthalene" from Tokyo Gas Co., Ltd. (sulphur content 0.05 per cent.) and 6.25 g. (25 per cent. of the naphthalene) of the dry earth were mixed and charged in a glass tube of 50–70 cm. in length and 2 cm. in diameter. The tube was sealed and heated in an electric furnace. The earth used had been dried at 120° for one hour, powdered, sifted with a sieve of 200 meshes, and heated once more at 300° for one hour. The temperature of the furnace was gradually raised to 300° in the course of just one hour and a half and maintained there for one hour. Then the electric current was cut off and the furnace was left to cool down to room temperature. The content of the sealed tube was washed out with benzene, and filtered by a silk sack. The earth in the sack was then completely extracted with benzene in a Soxhlet apparatus for 8–30 hours. The two benzene extracts were united and filtered, the benzene was distilled off, and the residue was subjected to steam distillation to remove unchanged naphthalene. The resinous matter left behind in the distillation flask was collected, rinsed out with benzene if it sticked to the wall of the flask, in a small weighed beaker, and dried at 120° until a constant weight to 0.01 g. was obtained.

The Relation between the Yield of the Resinous Matter and Chemical Composition of the Acid Earth. Seven specimens of the acid earth were analysed on one hand and their catalytic activities under the "standard condition" were measured on the other hand. The results are shown in Table 1.

No relation between the chemical composition and the catalytic activity seems to be found out from Table 1. But, when we take the ratios of the percentages of other constituents to those of SiO_2 as shown in Table 2, distinct relations between them and the catalytic activities can be found: (1) the larger the value of Al_2O_3/SiO_2, the greater the catalytic activity; (2) the larger the values of CaO/SiO_2 and K_2O/SiO_2, the smaller the catalytic activity; and, (3) the values of Ig. loss/SiO_2, Fe_2O_3/SiO_2, and MgO/SiO_2 seem to have no relation to the activity.

Table 1.

Earth	Locality of production	Depth of deposit where sample was gathered (metres)	Chemical composition (%)								Yield of resinous matter (g.)
			Ignition loss	SiO_2	Al_2O_3[5]	Fe_2O_3	CaO	MgO	K_2O[4]	Total	
A	Isozawa	7	9.51	65.62	13.61	3.89	1.47	3.98	1.82	99.90	1.65
B	Isozawa	3	7.78	67.91	16.09	3.17	0.60	3.51	1.35	100.41	1.82
C	Itoigawa	6.5	10.45	68.18	14.95	2.53	1.11	1.20	1.02	99.44	1.86
D	Odo-Sekiba	4.5	6.98	72.34	13.73	3.37	1.18	1.28	1.04	99.92	1.90
E	Odo-Sekiba	1.2	8.84	65.69	18.47	2.65	0.79	2.08	1.17	99.69	2.10
F	Itoigawa	Commercial	6.87	67.04	17.71	1.57	0.49	4.99	0.63	99.32	2.23
G	Itoigawa	0.9	11.50	58.92	20.13	3.05	0	3.15	0.95	97.70	2.60

Table 2.

Earth	$\frac{\text{Ig. loss}}{SiO_2}\times 100$	$\frac{Al_2O_3}{SiO_2}\times 100$	$\frac{Fe_2O_3}{SiO_2}\times 100$	$\frac{CaO}{SiO_2}\times 100$	$\frac{MgO}{SiO_2}\times 100$	$\frac{K_2O}{SiO_2}\times 100$	Yield of resinous matter(g.)
A	14.5	20.7	5.93	2.24	6.07	2.77	1.65
B	11.5	23.7	4.67	0.88	5.17	1.99	1.82
C	15.3	21.9	3.71	1.63	1.76	1.50	1.86
D	9.7	19.0	4.66	1.63	1.77	1.44	1.90
E	13.5	28.1	4.03	1.20	3.17	1.78	2.10
F	10.1	26.4	2.33	0.60	7.44	0.94	2.23
G	19.5	34.2	5.18	0	5.35	1.61	2.60

The problem was then attacked from another side; each constituent was considered separately and investigated on its catalytic activity for naphthalene.

SiO_2 and Al_2O_3. Silicic acid gel and aluminum hydroxide prepared by various methods were examined in the first place. The results are shown in Table 3.

(4) Na_2O was weighed together with K_2O.

(5) It has been already pointed out by Okazawa that Al_2O_3 content is always larger in the upper layers of Japanese acid earth deposits than in the lower, which may be noticed here again. (*Bull. Inst. Phys. Chem. Research, Japan*, **7** (1928), 977.)

Table 3.

	Method of preparation	Yield of resinous matter (g.)	Remarks
SiO_2 gel	(a) Dil. solution of $Na_2Si_2O_5 \cdot 2H_2O$ into 2.8 N nitric acid.	0.03	The quantity of the catalyst, 12.5 g. instead of 6.25 g. Standard condition in other respects.
	(b) Dil. solution of water glass into dil. hydrochloric acid.	0.06	Under the standard condition.
	(c) Ferric chloride solution into water glass solution. (Holmes's gel)[6]	0.03	,,
	(d) Holmes's gel washed with hydrochloric acid.	0.01	,,
$Al(OH)_3$[7]	(a) Clay was treated with sulphurous acid and resulting aluminium sulphite was decomposed by boiling.	0.00	The quantity of the catalyst, 12.5 g.
	(b) Dil. aqueous ammonia into dil. solution of aluminium nitrate.	0.02	Under the standard condition.
	(c) Dil. aqueous ammonia into dil. solution of aluminium chloride.	0.00	,,

As shown in Table 3, all the specimens of silicic acid gel and aluminium hydroxide used alone manifest no or quite poor activity. But when the two substances are mixed together in a suitable manner, a remarkable amount of the resinous matter is produced, the activity of the mixed catalyst becoming comparable to that of the acid earth.

Silicic acid gel (a) and aluminium hydroxide (b) of Table 3 are suspended in water separately, about 0.2 g. as SiO_2 or Al_2O_3 being contained per 10 c.c., and the two suspensoids are mixed in a porcelain basin, and evaporated to dryness on the water bath under stirring. The dried mass is powdered, treated as the "standard condition" requires, and tested on its catalytic activity. The yield of the resinous matter produced by the mixed catalyst thus obtained are plotted against the composition of the mixture in Fig. 1. The "standard condition" was adopted in the experiments except that 5.00 g., instead of 6.25 g., of the mixed catalyst was always taken.

Fig. 1 shows that there is a maximum in the catalytic activity in the neighbourhood of the composition, 35 per cent. Al_2O_3 and 65 per cent. SiO_2,

(6) Holmes, *Ind. Eng. Chem.*, **17** (1925), 280; ibid., **18** (1926), 386.
(7) Aluminium hydroxide, as it is very troublesome to wash completely, was finally purified by electro dialysis.

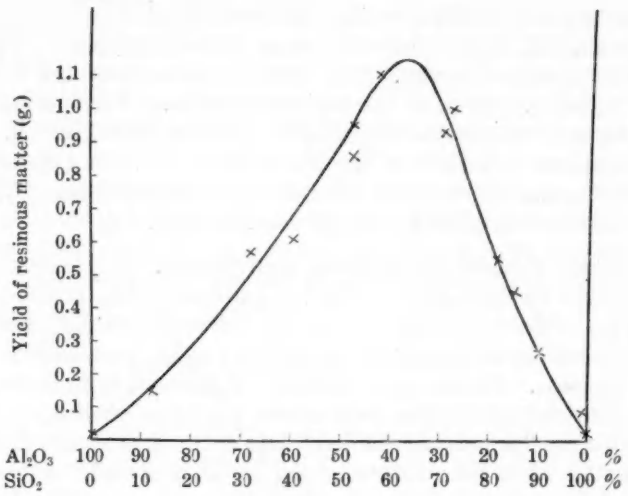

Fig. 1.

which corresponds to $Al_2O_3 \cdot 3SiO_2$. Its position, however, may be shifted according to the method of the preparation of silicic acid gel and aluminium hydroxide and the manner of mixing them. Moreover, it is not explicit whether any definite compound is formed by the simple mixing of the two, and, even if it is actually formed, it cannot be at once taken for granted that its composition and that of the constituent of the acid earth possessing the catalytic activity are identical. Notwithstanding that, it is evident that the co-existence of SiO_2 and Al_2O_3 is essential to the catalysis, and at any rate it is possible to prepare a catalyst with the activity comparable to that of the acid earth by the simple mixing of the above mentioned two substances, each of which is an extremely weak agent for the action when used alone, and the parallelism between the values of Al_2O_3/SiO_2 and catalytic activities shown in Table 2 seems to be not unreasonable from the above experimental results.

As already stated, if the acid earth contains free colloidal silica, the catalytic activity of such an earth with a comparatively small content of Al_2O_3 may be raised by adding aluminium hydroxide to it, for catalytically active centres may be newly formed. On the contrary, the addition of silica gel would result only in the dilution of the catalyst and cause the lowering of activity. Experimental results are in close agreement with the above speculation. The acid earth (A) of Table 1 was kneaded with a little water to a paste, diluted with water, and fresh aluminium hydroxide (as

Al_2O_3 about 10 per cent. of the weight of the earth dried at 300°) suspended in water was added to it. The whole was then evaporated to dryness on the water bath under stirring. This mixture used under the "standard condition" yielded 1.95 g. of the resinous matter. The increase in the yield of the product is about 20 per cent. (refer to Table 1 and 2). By the similar treatment the activity of the acid earth (C) of Table 1 was raised by about 15 per cent., whilst it was lowered by about 6 per cent., when the earth was mixed with silica gel (10 per cent. as SiO_2).

Hydroxides of Alkali and Alkaline Earth Metals. As stated above, the larger the ratios CaO/SiO_2 and K_2O/SiO_2 the smaller is the catalytic activity. It seems very probable, therefore, that the hydroxides of alkali and alkaline earth metals behave as poisons to the catalysts, and, as a matter of fact, this was the case. To the acid earth (F) of Table 1, a dilute solution of sodium hydroxide was added and the whole was evaporated up under stirring. Under the "standard condition" this contaminated catalyst gave no resinous matter when the quantity of the added hydroxide amounted to 5 per cent. of the weight of the dry earth, the catalytic activity being thus destroyed entirely, while the depression of the activity was 10 per cent. on the addition of 1 per cent. of the hydroxide. The acid earth (E) mixed with 3 per cent. of sodium hydroxide gave only 0.03 g. of the resinous matter (the depression is more than 98 per cent.). Potassium hydroxide is a stronger poison; with 1 per cent. of the hydroxide the activity of the earth (D) was lowered by about 20 per cent.

The action of the hydroxides of alkaline earth metals is milder; the acid earth (F) with 5 per cent. (as CaO) of calcium hydroxide gave 0.24 g. of the resinous matter, the depression of the activity being about 90 per cent., and with 3 per cent. of CaO the activity of the acid earth (F) was lowered by about 50 per cent. The intensity of the poisoning by barium hydroxide is nearly equal to that by calcium hydroxide.

It was further observed that, when the poisoned earth was treated with hydrochloric acid, it recovered the original activity completely.

Ferric and Magnesium Hydroxides. As seen from Table 2, the value of neither Fe_2O_3/SiO_2 nor MgO/SiO_2 has parallelism with the catalytic activity. It may be therefore anticipated that ferric and magnesium hydroxides are indifferent to the catalytic action.

Each hydroxide, prepared by the interaction of the nitrate and aqueous ammonia, washed with a large quantity of water, and purified finally by electro-dialysis, was suspended in water and added to the acid earth. The decrease in the yield of the resinous matter just matches that caused by the dilution of the catalyst as in the case of silica gel.

It was also found that no resinous matter was produced by the use of a mixture of silica gel and ferric hydroxide ($SiO_2 : Fe_2O_3 = 3:4$) and, as already stated, Holmes's silica gel containing ferric hydroxide prepared from water glass and ferric chloride manifested almost no activity. From the above results, it may be safely granted that Fe_2O_3 and MgO are the simple diluents of the catalyst.

Thus, it appears that the rôles played by the chief constituents of Japanese acid earth in its catalytic action on naphthalene are fully explained and experimental results are in close agreement with the expectation. Water plays also an important part in the catalysis and its action will be discussed in details in another communication.

The Activities of Several Substances other than Japanese Acid Earth. Several other substances were analysed and examined on their catalytic activities on naphthalene by the same method. The data of experiments are shown in Table 4.

Table 4.

Substance	Locality of production	Chemical composition (%)								Yield of resinous matter (g.)
		Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Total	
Bentonite	Japan	7.22	63.30	20.30	3.00	1.12	0.54	3.38	98.89	0.25
Caoline	Japan	12.42	50.19	32.79	3.10	0.35	0	1.34	100.19	0.81
Clay I	Manchukuo	13.87	45.38	34.29	4.80 (+ TiO_2)	1.43	1.11	—	—	0.33
Clay II	Manchukuo	14.54	43.56	40.36	2.21 (+ TiO_2)	0.79	0.34	0.95	102.75	0.20
Diatom earth	Japan	5.10	80.70	11.90	3.90	0	0.20	0	101.80	0.22
Bauxite	India	12.87	1.22	74.78	10.35 (+ TiO_2)	0.49	0.16	—	—	0
Active charcoal	Germany	—	—	—	—	—	—	—	—	0

All the substance, which contain SiO_2 and Al_2O_3 as their chief constituents, possess more or less the catalytic activity on naphthalene.

According to Shigemune[8], Japanese bentonite much resembles Japanese acid earth in its chemical composition, adsorptive powers for dyestuffs, and in many other respects, while Table 4 shows that its catalytic activity is only about one tenth of that of the acid earth. In the authors' opinion, its poor activity may be attributed to the comparatively large contents of CaO

(8) *Reports of Tokyo Imperial Industrial Research Laboratory*, **25** (1930), No. 10.

and K_2O, both the strong poisons to the catalysis, and therefore, if these poisons be removed, the activity may be raised. On treating the acid earth with hydrochloric acid, its composition as well as its catalytic activity suffers little change. In the case of bentonite, however, the ratio $CaO+K_2O/SiO_2$ is greatly diminished by the same treatment (in this respect there is a distinct difference between the two) and simultaneously its activity is raised enormously as shown in Table 5, exceeding even the greatest value of the acid earth given in Table 1. This result seems to be anticipated if the data given in Table 2 and 5 are compared, and bentonite is regarded as a species of the acid earth so far as the catalytic action is concerned.

Table 5.

Catalysts		$\frac{\text{Ig. loss}}{SiO_2}\times100$	$\frac{Al_2O_3}{SiO_2}\times100$	$\frac{Fe_2O_3}{SiO_2}\times100$	$\frac{CaO}{SiO_2}\times100$	$\frac{MgO}{SiO_2}\times100$	$\frac{K_2O}{SiO_2}\times100$	Yield of resinous matter (g.)
Earth F	Before treatment with HCl	10.1	26.4	2.33	0.60	7.44	0.94	2.23
	After treatment with HCl	9.79	25.7	1.32	0.73	6.08	0.66	2.33
Bentonite	Before treatment with HCl	11.4	32.1	4.74	1.77	0.85	5.34	0.25
	After treatment with HCl	10.9	36.0	3.31	0.77	1.08	1.21	2.89

Further experiments were carried out to ascertain whether SiO_2 and Al_2O_3 could be replaced by TiO_2 and La_2O_3 respectively or not, and the combinations of TiO_2-Al_2O_3 and SiO_2-La_2O_3 were tested on the catalytic action. No resinous matter was found to be produced in both cases. Some interesting results might be attained if the above experiments be extended to various other metallic oxides.

Summary.

(1) Rôles played by the chief constituents of Japanese acid earth in its catalytic action on naphthalene have been studied. It has been found that the co-existence of SiO_2 and Al_2O_3 is essential to the catalysis and hydroxides of alkali and alkaline earth metals behave as poisons to the catalyst, while ferric and magnesium hydroxides are indifferent to the catalysis.

(2) Several substances other than Japanese acid earth, which contain SiO_2 and Al_2O_3 as their chief constituents, have been also examined on the same catalytic action.

(3) It has been tested whether TiO_2 and La_2O_3 can be substituted for SiO_2 and Al_2O_3 respectively in the catalytic action or not.

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THE SURFACE TENSIONS OF ETHYL ALCOHOL AND CARBON DISULPHIDE AT LOW TEMPERATURES.

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The surface tensions of some organic compounds were measured by the method of capillary rise by one of the present writers and were communicated in this Bulletin.[1] The present paper contains the results of the further measurements with ethyl alcohol and carbon disulphide. The details of the measurements were mentioned in the previous paper.[1]

Ethyl alcohol and carbon disulphide used in the present measurements were the pure chemicals from Kahlbaum and purified in the usual ways. Their boiling points were 78.26°C. (759.5 mm.) and 46.00–46.10°C. (760.7mm.) respectively.

The experimental results are shown in Table 1 and 2 and diagrammatically in Fig. 1 and 2. The formula given at the bottom of each table has been obtained from the experimental data by the method of the least squares, and expresses the relation between temperature and surface energy, τ in the formula for carbon disulphide being the temperature measured from the critical temperature, 277.7°C.[2] The formula for ethyl alcohol is quadratic and not of Eötvös type, for it is considered to have anomalous properties in several respects just like methyl alcohol dealt with in the previous paper. From these formulae the surface tensions at the corresponding temperatures have been calculated and are given in the sixth columns of the tables.

(1) Tonomura and Chujo, this Bulletin, **7** (1932), 259.
(2) Landolt-Börnstein's Tables, 5th ed. (1923), Vol. 1, 261.

Table 1.

The Surface Tension of Ethyl Alcohol.

Temp. °C.	Height cm.	Radius cm.	Density $D^{(4)}-d^{(3)}$	Surface Tension Dynes/cm.		Capillary
				σ (obs.)	σ (calc.)	
30.00	2.201	0.02498	0.7810	21.14	21.22	B
20.00	1.530	0.03692	0.7894	22.00	22.00	A
−12.16	2.523	0.02497	0.8166	25.30	25.19	B
−22.02	2.576	0.02498	0.8250	26.10	26.10	B
−31.49	1.789	0.03692	0.8332	27.15	27.04	A
−43.21	2.708	0.02498	0.8453	28.11	28.32	B
−52.83	2.786	0.02497	0.8517	29.12	29.27	B
−62.49	1.926	0.03692	0.8602	30.17	30.29	A
−69.75	2.905	0.02497	0.8667	30.90	31.06	B
−74.73	1.989	0.03692	0.8710	31.54	31.59	A
−80.52	2.995	0.02497	0.8762	32.21	32.22	B
−89.09	3.054	0.02497	0.8838	33.12	33.17	B
−93.08	2.083	0.03692	0.8874	33.64	33.61	A

$$\sigma\left(\frac{M}{D}\right)^{\frac{1}{3}} = 703.09 - 1.3901T + 0.00043187T^2$$

Table 2.

The Surface Tension of Carbon Disulphide.

Temp. °C.	Height cm.	Radius cm.	Density $D^{(5)}-d^{(6)}$	Surface Tension Dynes/cm.		Capillary
				σ (obs.)	σ (calc.)	
20.00	2.089	0.02497	1.2617	32.38	32.33	B
10.00	2.152	0.02497	1.2772	33.76	33.89	B
−1.85	1.510	0.03691	1.2939	35.66	35.75	A
−11.98	1.567	0.03691	1.3082	37.42	37.37	A
−14.43	1.576	0.03692	1.3117	37.69	37.76	A
−14.65	2.354	0.02497	1.3120	37.93	37.79	B

(3) Landolt-Börnstein's Tables, 5th ed. (1923), Vol. 1, 271.
(4) International Critical Tables, Vol. 3, 27.
(5) Ibid., 23.
(6) Landolt-Börnstein's Tables, 5th ed. (1923), 281.

Table 2. (*Concluded*)

Temp. °C.	Height cm.	Radius cm.	Density $D-d$	Surface Tension Dynes/cm.		Capillary
				σ (obs.)	σ (calc.)	
−21.29	1.613	0.03691	1.3214	38.85	38.87	A
−24.80	2.427	0.02497	1.3265	39.53	39.43	B
−29.93	2.467	0.02498	1.3338	40.42	40.27	B
−31.47	1.669	0.03691	1.3359	40.63	40.53	A
−41.80	2.539	0.02497	1.3506	42.10	42.22	B
−42.39	1.725	0.03691	1.3514	42.47	42.32	A

$$\sigma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 2.0007\ (\tau - 9.28)$$

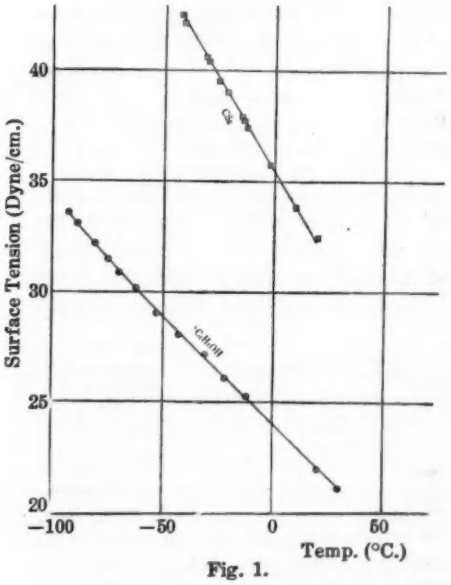

Fig. 1.

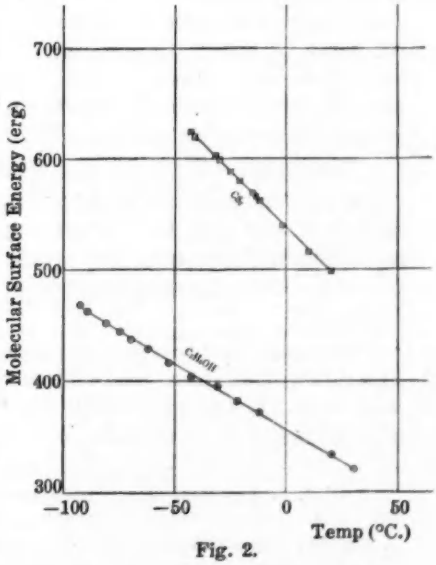

Fig. 2.

The writers wish to express their hearty thanks to Prof. S. Mitsukuri for his suggestion and guidance.

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THE CHEMICAL CHANGE OF CARBON DISULPHIDE UNDER ELECTRODELESS DISCHARGE.*

By Misao EMI.

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There have been many investigations to prepare carbon monosulphide,[1] among which the work by J. Dewar and H. O. Jones appears to be the most important. They decomposed the vapour of carbon disulphide at a low pressure of about 15 mm. under silent discharge in an ozonizer.

The present author decomposed the vapour of carbon disulphide under electrodeless discharge and examined the change. The vapour was passed through a discharge apparatus, and to attain a pressure sufficiently low to effect electrodeless discharge, a bulb containing carbon disulphide was connected with the reaction vessel by means of a long capillary tube with a diameter of about 0.1 mm., and the vapour coming out of the reaction vessel was condensed by cooling with liquid air, so that carbon disulphide distilled continuously through the reaction vessel. Further details of the apparatus are shown in Fig. 1.

Electrodeless discharge was effected by connecting two annular copper stripes on the reaction vessel to a supply of an alternating current of a frequency of approximately 10^7 cycles per second, which was generated from an alternating current of 200 cycles per second and about 2000–3000 volts by using a small transmitting valve. The circuit is shown diagramatically in Fig. 2.

To purify carbon disulphide (from Hopkin and William Co., Ltd.), it was first distilled at about 46°, shaken with concentrated sulphuric acid, then with mercury, and finally with lime, and redistilled at 46°. When carbon disulphide (50 c.c.) was placed in bulb A and the bulb was cooled in ice, the

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* Cf. J. J. Thomson, The Electrodeless Discharge through Gases, *Phil. Mag.*, Nov. 1927; J. S. Townsend and R. H. Donaldson, Electrodeless Discharge, *Phil. Mag.*, Jan. 1928; G. Mierdel, Untersuchungen über den Elektrodenlosen Ringstrom. *Ann. Physik*, Nr. 5, 1928; S. B. Bhatnager and Rama Krishna Sharma, Chemical Reaction under Electrodeless Discharge, *J. Indian Chem. Soc.*, June, 1928.

(1) M. Berthelot, *Ann. chim. phys.*, (3), **53** (1858), 142; A. W. Hofmann, *Ber.*, **3** (1870), 197; T. Sidot, *Compt. rend.*, **69** (1869), 1303; S. M. Losanitsch, *Ber.*, **30** (1897), 135; **40** (1907), 4656; J. Thomsen, *Z. anorg. Chem.*, **34** (1903), 187; A. Deninger, *J. prak. Chem.*, **51** (1895), 346; J. Dewar and H. O. Jones, *Proc. Roy. Soc.*, A, **83** (1910), 408, 526; **85** (1911), 574. Further cf. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VI, p. 94.

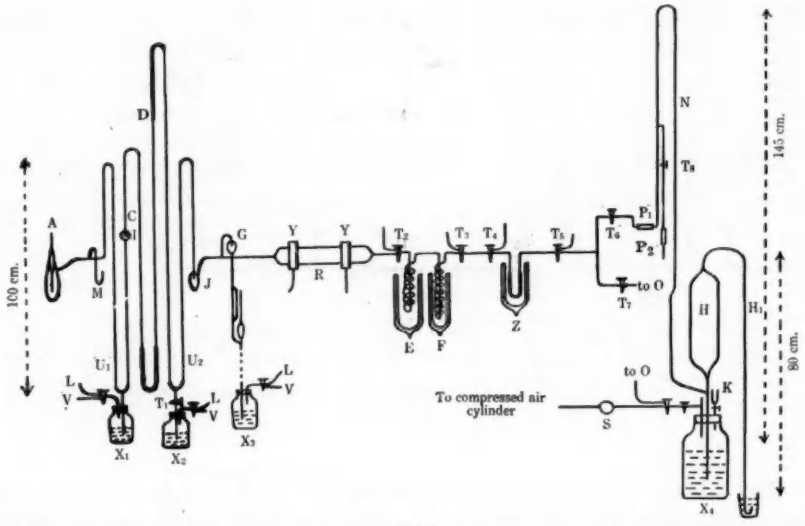


Fig. 1. A: bulb containing carbon disulphide. M: manometer. CD: capillary tube. I and J: traps for mercury. GX_3: McLeod guage. R: reaction vessel (about 250 c.c.). Y: annular copper stripes. E and F: condensers. Z: spare condenser. T_1, T_2, T_3, T_4, T_5, T_6, T_7 and T_8: taps. Condensed carbon disulphide is removed from T_2, T_3, T_4 and T_5. The vapour of carbon disulphide attacks tap grease, and hence it is necessary to grease the taps frequently to avoid leaks. HX_4: Toepler pump to drive the gas from H into capillary tube H_1. X_1, X_2, X_3 and X_4: mercury reservoirs. K: funnel for supplying mercury to keep the mercury level of X_4 constant. S: safety valve. O: Cenco Hyvac pump. It is necessary to apply a pressure of about 600 mm., and tube N extends to about 145 cm. above the mercury level in X_4. Compressed air is used to expel the gas from cylinder H, the pressure being controlled to about 0.8 atmosphere by safety valve S. U_1 and U_2: long glass U-tubes for controlling the flow of the gas. L's: air is supplied by L's. The air is dried with $CaCl_2$, conc. H_2SO_4, potash, and finally with P_2O_5. V's: The air in the reservoirs is sucked from V's. Mercury goes up to the bottom of U_1 or U_2 and stop the flow of the gas when air is allowed from L, and goes down into the reservoir when air is sucked from V. P_1 and P_2: tubes for drying the gas and the air flowing to Toepler pump respectively.

vapour pressure was found 128 mm. mercury, which was higher than the values obtained by H. V. Siemens (127 mm.) and by Henning and Stock (127.25 mm.).

To fill bulb A with carbon disulphide, the bulb was communicated with a Cenco Hyvac pump through a phosphorus pentoxide tube, evacuated, and dried, and liquid carbon disulphide was put in. After carbon disulphide having been frozen by cooling in liquid air, the bulb was evacuated through the phosphorus pentoxide tube as far as possible, and then sealed off.

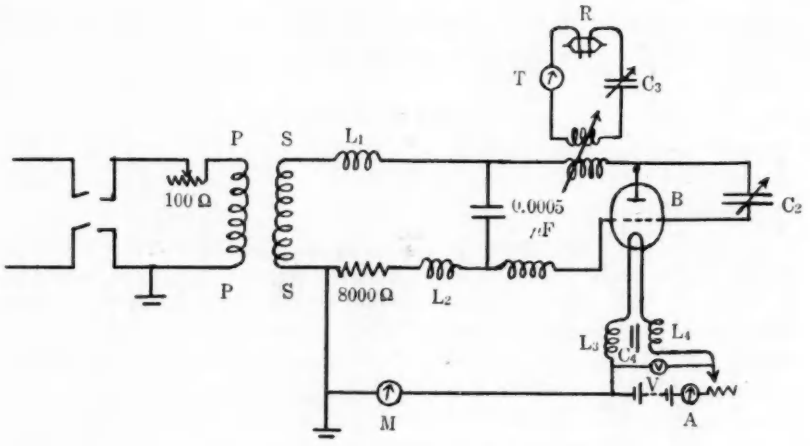


Fig. 2. L_1, L_2: pyrex tubes of 2′ 6″ length and $1\frac{1''}{8} - 1\frac{1''}{4}$ diameter, 2′ being wound with D.S.C. copper wire of 32 S.W.G. L_3, L_4: one pyrex tube of $1\frac{1''}{2}$ diameter and 16″ length, wound doubly with D.C.C. copper wire of 16 S.W.G. C_4: glass tube with copper foil on its inner wall to slide inside the tube of L_3 and L_4. C_2, C_3: variable condensers, each consisting of two copper sheets of $4'' \times 4'' \times \frac{1''}{16}$, mounted on pillars so that the space between them can be adjusted. M: milliammeter (0—30 m.a.). T: thermoammeter (0—12 amp.). B: Marconi valve (12.5 volts, 5.5 amp.). P: primary coil of the transformer. S: secondary coil of the transformer. R: reaction vessel. A: ammeter (0—10 amp.). V: voltmeter (0—15 volts).

U_1, U_2, T_2, T_3, T_4, T_5 and T_6 were then all communicated with the Toepler pump, and condenser E was placed in liquid air, and thus the vapour of carbon disulphide was allowed to flow from bulb A and to carry any residual air with it, the pump removing continuously the carried air. It took a long time (about two days) to expel air from the apparatus because of the slowness of the flow of the gas.

The vapour of carbon disulphide in the apparatus was tested on purity in the following manner. U_1 and U_2 were shut, condenser E previously evacuated as highly as possible was placed in liquid air, and taps T_2 and T_3 were then shut. The mercury in the McLeod guage was allowed to rise by adjusting the pressure in the mercury reservoir X_3 to the atmospheric pressure. U_1 and U_2 were then opened; in 5 minutes the mercury fell by 50 mm., and then U_1 was shut and T_2 opened. In about 10 minutes U_2 was shut and the pressure was read on the guage during about half an hour, and found constant at 0.005 mm. The initial pressure of the carbon disulphide in the

reaction vessel being 50 mm., the ratio of the pressure of air to that of carbon disulphide can not be greater than 0.005/50, that is 0.01 per cent.

The pressure of the vapour of carbon disulphide in the reaction vessel in the steady state was determined in the following manner. The whole apparatus was evacuated to about 0.005 mm., and the vapour of carbon disulphide was allowed to flow from bulb A cooled in ice (the vapour pressure being 128 mm. here) into the apparatus. Condenser E was then cooled in liquid air and the pressure was read, Table 1.

Table 1.

Time (min.)	Pressure (mm.)
0	0.08
5	,,
10	,,
15	,,
20	,,
25	,,
35	,,

Table 2.

Time (min.)	Pressure (mm.)	Time (min.)	Pressure (mm.)	Time (min.)	Pressure (mm.)
0	0.085	30	0.0925	60	0.075
4	,,	35	,,	65	,,
9	,,	40	,,	72	,,
15	0.0925	45	,,	80	,,
20	,,	50	0.075	88	,,
25	,,	55	,,	90	,,

When the pressure in the apparatus was steady (0.08 mm.), condenser F as well as E was cooled in liquid air, and the vapour of carbon disulphide was subjected to the action of electrodeless discharge. The pressure was read continually, Table 2. The pressure fell to 0.075 mm. in fifty minutes and stayed steady there.

When electrodeless discharge was stopped, the whole wall of the reaction vessel was found to be covered with brown solid, and the narrow necks with dark solid. On removing liquid air from condenser E, instantaneous detonation took place with a flash, and the upper part of the condenser was covered with a dark lustrous solid mass, and the bottom with a dark brown powder, while no liquid was found.

A part of the deposit on the wall of the reaction vessel was dissolved in carbon disulphide, when a brown solution resulted. On adding a drop of concentrated sulphuric acid to this solution, a brown precipitate was formed. The deposit on the bottom of condenser E was dissolved in carbon disulphide to a purplish brown solution, which gave a purple precipitate on adding a drop of concentrated sulphuric acid. These solid substances appear to be the polymers of gaseous carbon monosulphide in different degrees of polymerization.

The black lustrous substance on the wall of the reaction vessel may probably be a polymer of carbon ditrita-sulphide $(C_3S_2)_x$ which might be formed together with the polymers of monosulphide. It seems that mercury also deposited on the wall of the condenser.

It can not be said that carbon monosulphide CS existed as a stable gas. It is very interesting that Dewar and Jones, too, reported the formation of a brown mass accompanied by a flash and detonation. More precise and quantitative investigation will further be made.

In conclusion the author wishes to express his hearty thanks to Prof. F. G. Donnan of the University College, London, where this investigation was made by virtue of his kind suggestion and encouragement, and to acknowledge the kind advice and great help rendered by Dr. R. W. Lunt during the course of the experiments.

RELATION BETWEEN THE TEMPERATURE AND THE *p*H VALUE OF THE BOTTOM DEPOSITS FROM POND TAKASUKANUMA.

By Ken SUGAWARA.

Received August 13th, 1934. Published October 28th, 1934.

Knowledge of the relation between the temperature and the *p*H value of lake deposits is important to biological and biochemical studies of them. If a sample of deposits manifests different *p*H values at different temperatures, such will natu ally have different *p*H values also in the bottom of the lake as the temperature varies along with the seasons. Such a variation of *p*H may, on one hand, have seasonal influence on the benthoic fauna and flora, and, on the other, it may affect the chemical changes taking place in the bottom.

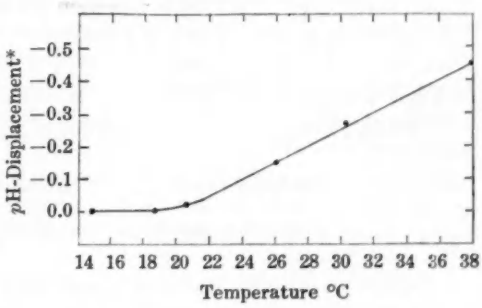
Now, the measurement of the *p*H value of bottom deposits is practically made in the laboratory instead of on the spot. Then, it happens very often that the temperature of the laboratory differs from that of the spot, and the observed values must be corrected in order to obtain the real values.

When the author made the investigation of the annual variation of the *p*H value in the deposits of Pond Takasukanuma in the course of the years

1932 to 1933, in parallel with studies on other factors affecting deposit metabolism,[1] it was necessary to establish the relation between the temperature and the *p*H value.

Displacements of the *p*H value between two temperatures were measured in five experiments. The results are shown in the table, by aid of which a curve of temperature-*p*H-displacement was drawn. This curve serves to compute the *p*H value of the actual place from that observed in the laboratory. Thus, on the 9th of August, 1933, the temperature was read 31.0°C. in laboratory and 14.9°C. in the bottom of the lake, and the observed value *p*H 6.46 is reduced to 6.73 by correction of +0.27.

	Temp. °C.	*p*H	*p*H-displacement
I	15.4	6.68	0.01
	19.8	6.67	
II	14.8	6.16	0.02
	20.7	6.14	
III	18.8	6.48	0.15
	26.0	6.33	
IV	18.8	6.52	0.26
	30.5	6.26	
V	19.1	6.83	0.45
	38.0	6.38	



* Referring to the *p*H value of the horizontal part of the curve below about 18.7°C.

It is remarkable that the curve runs horizontally below 18.7°C., and that the horizontal part seems to extend further as the curve runs below 14.8°C., the lowest temperature of the experiments. This leads to the supposition that the bottom deposits are so conditioned, at least in the particular case of the deepest part of Pond Takasukanuma, that the *p*H value remains constant, so far as the dissociation equilibrium in it is concerned, because the temperature of that part of the bottom does not exceed 17.5°C. throughout the whole year, as stated in the report cited.

It is of question whether these relations obtained can be applied in general to any type of lakes and to any part of their bottoms. In fact, even in Takasukanuma, the bottom is warmed to a higher temperature in its shallower part, and it is highly possible that *p*H varies with the seasons solely owing to dissociation equilibrium.

Studies will be continued further along these lines.

(1) *Japanese Journal of Limnology*, Vol. IV. No. 4.

Experimental.

Thoroughly kneaded sample (1 c.c.) is well stirred with 2 c.c. of distilled water for one minute, then a knife-tipful of quinhydrone is added and the mixture is stirred further for half a minute. A platinum electrode is inserted and pH is measured in 3 minutes potentiometrically referring to the saturated calomel half cell.

Chemical Laboratory, Tokyo High School.

THE CONSTITUTION OF THE HYDROXY-DERIVATIVES OF DIPHENYLENE OXIDE OBTAINED FROM RESORCINOL.

By **Kiyoharu TATEMATSU** and **Bennosuke KUBOTA.**

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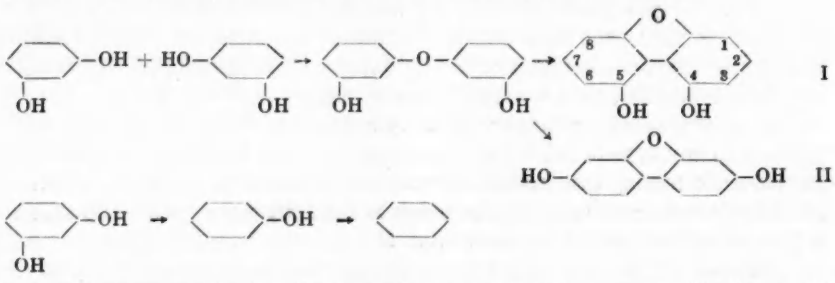
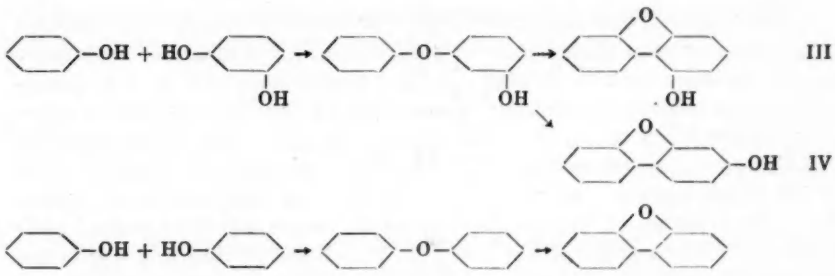
It was previously reported[1] that resorcinol undergoes a certain reduction and condensation under the influence of the blue oxide of tungsten at 500–550°, and gives two substances besides benzene, phenol, and diphenylene oxide. Of the two substances, one melting at 138–138.5° was assumed by Y. Tsuzuki to be 4-hydroxydiphenylene oxide (III) from the observation of its decomposition product as well as of absorption spectra, and the other melting at 241–242° was considered 4,5-dihydroxydiphenylene oxide (I). The process of the reactions giving these two compounds appeared to be represented by the dotted arrows in the scheme shown below:



(1) B. Kubota, Y. Fujimura, and K. Akashi, *Scientif. Pap. Inst. Phys. Chem. Research, Japan*, **2** (1925), 185; Y. Tsuzuki, ibid., **6** (1927), 301.



With the view of ascertaining the constitutions of these compounds the monohydroxydiphenylene oxide melting at 138–138.5° was again examined. It was compared with 2-hydroxydiphenylene oxide obtained by us from Cullinane's 2-aminodiphenylene oxide[2] by means of the diazo-reaction. The acetyl-, methyl-, and dinitro-derivatives of them were also compared. As shown in Table 1, the melting points of the monohydroxydiphenylene oxide from resorcinol and its derivatives are in good agreement with those of the corresponding compounds obtained from 2-aminodiphenylene oxide, and moreover, the mixed melting point of the two monohydroxydiphenylene oxides gave no depression.

Table 1. Comparison of the Melting Points.

Substance	From resorcinol	From 2-amino-diphenylene oxide
Hydroxydiphenylene oxide	138–138.5°	138–138.5°
Acetyl-derivative	111–111.5°	111–111.5°
Methyl-derivative	93–94°	97–97.5°
Dinitro-derivative	216–217° (decomp.)	216.5–217° (decomp.)

These facts indicate evidently that the compound in question obtained from resorcinol is none other than 2-hydroxydiphenylene oxide (IV), and may naturally suggest that the other substance obtained from resorcinol, melting at 241–242°, is more probably 2,7-dihydroxydiphenylene oxide (II). Although the latter problem is yet under investigation, the main processes of the reactions may be represented by the real arrows in the scheme shown above.

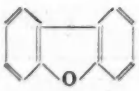
(2) N. M. Cullinane, *J. Chem. Soc.*, **1930**, 2267.

The comparative study of the absorption spectra was the chief ground of the previous arguments concerning the constitutions of these substances. As the previous authors pointed out, the absorption curve of 2-hydroxydiphenylene oxide has a striking resemblance in the form to that of *o*-hydroxydiphenyl but not to that of *p*-hydroxydiphenyl. But it is remarkable that this curve resembles that of 2,4-dihydroxydiphenyl and especially that of diphenylene oxide. As seen from the curves given in the experimental part, the influence of the hydroxyl-group on the absorption spectra is different with the position of the group in the diphenyl ring and also in the diphenylene oxide ring. Thus, if a hydroxyl-group is introduced to diphenyl in the ortho-position with respect to the diphenyl linkage, the absorption spectra are strongly influenced, while the effect of a para-hydroxyl-group is so weak that the form of the curve is hardly affected. From these points of view formula IV is highly probable for the monohydroxydiphenylene oxide melting at 138–138.5°.

Further the constitution of this compound was confirmed by studying its bromination product. Applying Kekulé's formula to the two benzene rings in diphenylene oxide, three formulae (1), (2), and (3), which are conditioned by the two possible arrangements of bonds in each benzene ring, may be considered :

(1)

(2)

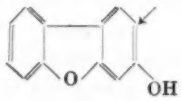


(3)

Two of them, (2) and (3), possessing respectively one and two double bonds common to the benzene and the furan rings should be under greater intramolecular strain, because two and four β intravalency angles are respectively included in the furan rings of them, and, therefore, according to Mills's hypothesis,[3] considerable distortion of the natural valency directions should be required to approximate these angles to the intravalency angle of the furan ring. In formula (1) in which single bonds only are common to the benzene and the furan rings, four α intravalency angles are brought into the furan ring, and as the α-angle does not differ from the intravalency angle of the furan ring so much as the β-angle does, the molecule of the form (1) should suffer less strain. Thus Mills's hypothesis indicates that the form (1) is the most stable constitution of diphenylene oxide. If our consideration is correct, the most stable form of 2-hydroxy-

(3) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, **1930**, 2510.

diphenylene oxide must be (4), and the substitution of bromine should take place mainly at the 3-position as indicated by the arrow :



(4)

We examined accordingly the action of bromine on 2-hydroxydiphenylene oxide, and as expected, the main product was 3-bromo-2-hydroxydiphenylene oxide. The orientation of the bromine atom in the bromo-2-hydroxydiphenylene oxide was established as follows:

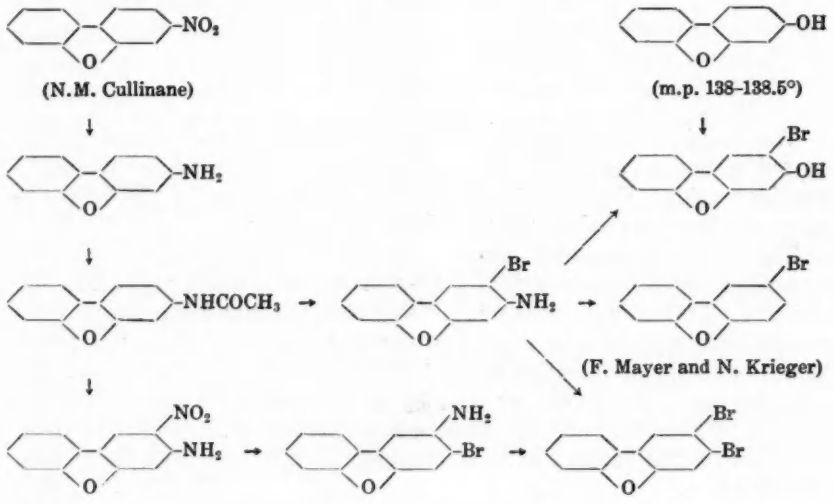
The bromo-2-aminodiphenylene oxide, which was obtained by bromination and subsequent hydrolysis of the 2-acetamino-compound prepared from Cullinane's 2-nitrodiphenylene oxide,[4] was changed into the corresponding bromo-2-hydroxydiphenylene oxide by the diazo-reaction, which was found identical with the bromination product of 2-hydroxydiphenylene oxide. On replacing the amino-group by hydrogen, the bromo-2-aminodiphenylene oxide gave 3-bromodiphenylene oxide of F. Mayer and W. Krieger.[5] Hence, the position of the bromine atom in the bromo-2-hydroxydiphenylene oxide is either 3 or 6.

2-Acetaminodiphenylene oxide, obtained by acetylation of the 2-amino-compound, gave a nitro-2-aminodiphenylene oxide on nitration and subsequent hydrolysis. This nitro-amino-compound was reduced to a diamino-compound, which proved to be an *o*-diamine, because it combined with benzil and phenanthrene-quinone to close a quinoxaline ring.[6] Hence, the position of the nitro-group must be either 1 or 3.

On replacing the amino-group by bromine and subsequently reducing the nitro-group, the nitro-2-aminodiphenylene oxide was converted into an amino-2-bromodiphenylene oxide. From this amino-2-bromodiphylene oxide and from the bromo-2-aminodiphenylene oxide mentioned above, Sandmeyer's reaction yielded the same dibromo-compound. Hence the nitro-group in the above-mentioned nitro-2-aminodiphenylene oxide and the bromine atom in the bromo-2-aminodiphenylene oxide, and consequently the bromine atom in the bromo-2-hydroxydiphenylene oxide, must be in the same position, and that in 3. Thus it was established that the main product of bromination of 2-hydroxydiphenylene oxide is 3-bromo-2-hydroxy-diphenylene oxide.

(4) N. M. Cullinane, loc. cit.
(5) *Ber.*, **55** (1922), 1659.
(6) W. Borsche and B. Schacke, *Ber.*, **56** (1923), 2498.

The above-mentioned nitro-2-aminodiphenylene oxide melting at 222° was supposed by Cullinane[7] to possess the nitro-group in the 1-position, but it was thus established that the nitro-group is in the 3-position.



Experimental.

(1) **2-Hydroxydiphenylene oxide.** 2-Nitro-diphenylene oxide is the main product of nitration of diphenylene oxide.[8] It was converted into 2-aminodiphenylene oxide by reducing with stannous chloride in glacial acetic acid saturated with hydrogen chloride. The product crystallized readily from dilute alcohol in colourless needles, m.p. 99–99.5° (W. Borsche and W. Bothe give 94°).

The sulphate of the 2-amino-compound, obtained by heating 2-amino-diphenylene oxide (12 g.) in 5% sulphuric acid (330 c.c.), was diazotized at 0° with sodium nitrite (4.5 g.) in water (12 c.c.), when the diazo-compound gradually separated out in brown yellow needles. After being allowed to stand over night at 0°, the product was gradually put into a boiling 50% copper sulphate solution (400 g.),[9] and the mixture was boiled in a flask with a reflux condenser for two hours. The diazo-compound which was

(7) N. M. Cullinane, loc. cit.
(8) W. Borsche and W. Bothe, *Ber.*, **41** (1908), 1940.
(9) D. R. P., 167211.

formerly said to be stable,[10] was thus decomposed, and the hydroxy-compound separated out in lustrous crystals. It was recrystallized from dilute alcohol, when it separated out in colourless plates melting at 138–138.5° (Yield 5 g.).

On adding a drop of ferric chloride solution to a solution of the substance, made by dissolving it in a very small quantity of alcohol and then adding water till the solution just began to become turbid, it gave a yellowish green colour, which turned light brown on addition of a dilute soda solution.

The acetyl-derivative, obtained by heating the hydroxy-compound with acetyl chloride, crystallized from concentrated acetic acid in large prisms melting at 111–111.5°.

The monomethyl-derivative, obtained by treating the hydroxy-compound with dimethyl sulphate and caustic soda solution, crystallized from dilute alcohol in plates, m.p. 97–97.5°. It melts somewhat higher than the methyl-derivative of the monohydroxydiphenylene oxide from resorcinol (93–94°).

The dinitro-derivative, obtained by nitration of the hydroxydiphenylene oxide in glacial acetic acid with concentrated nitric acid, crystallized from glacial acetic acid in small yellow prisms melting at 216–217° (decomp.).

These properties of the 2-hydroxydiphenylene oxide are in good agreement with those of the hydroxydiphenylene oxide described by the previous authors.[11] Moreover, the mixed melting of the two substances gave no depression, indicating the identity of the two substances.

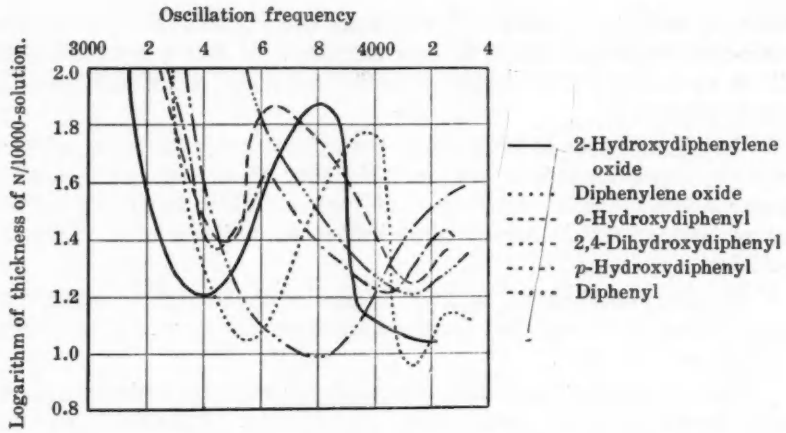
The absorption curves. The results of a comparative study on the absorption curves of hydroxdiphenylene oxide from resorcinol, its acetyl-derivative, diphenylene oxide, mono- and di-hydroxydiphenyls are shown in the figure. All observations of absorption spectra were made in alcoholic solution.

The curves of the 2-hydroxydiphenylene oxide from the 2-nitro-compound and its acetyl-derivative have not been drawn, for they coincide with the curves of the hydroxydiphenylene oxide from resorcinol and diphenylene oxide respectively.

As already pointed out, the form of the curve of the hydroxy-compound probably depends chiefly upon the diphenylene oxide ring, and the position of the hydroxyl-group is not to be decidedly determined by this result only.

(10) W. Borsche and W. Bothe, loc. cit.

(11) B. Kubota, Y. Fujimura, and K. Akashi, loc. cit.; Y. Tsuzuki, loc. cit.



(2) 3-Bromo-2-hydroxydiphenylene oxide from 2-hydroxydiphenylene oxide. Bromine (0.5 g.) dissolved in glacial acetic acid (1 c.c.) was added drop by drop at 0° to a solution of 2-hydroxydiphenylene oxide (0.6 g.) in the same solvent, and two hours later a large quantity of water was poured, when a white crystalline precipitate was formed. It was recrystallized from dilute acetone, colourless needles melting at 113°–113.5° (Yield 0.65 g., 70% of the theoretical). Treated with dimethyl sulphate and a caustic soda solution, this compound gave a methyl-derivative melting at 147–148°.

(3) 3-Bromo-2-hydroxydiphenylene oxide from 2-acetaminodiphenylene oxide. (i) *2-Acetaminodiphenylene oxide.* 2-Nitrodiphenylene oxide was reduced to 2-aminodiphenylene oxide by the action of stannous chloride in acetic acid saturated with hydrogen chloride. The amino-compound (3 g.) was dissolved in absolute alcohol (30 g.) and to this solution acetic anhydride (15 g.) was added. After being kept for half an hour at ordinary temperature, the solvent was evaporated on the water bath. The operation of adding alcohol and evaporating was repeated until a white crystalline mass was obtained. It was recrystallized from dilute alcohol, colourless flat needles melting at 176.5–177° (Yield 3 g.).

(ii) *3-Bromo-2-acetaminodiphenylene oxide.* 2-Acetaminodiphenylene oxide (0.8 g.) was dissolved in glacial acetic acid (15 c.c.) and bromine (0.6 g.) in the same sovent (1.5 c.c.) was added at room temperature, when the colour of bromine soon disappeared and a white crystalline precipitate separated out. After an hour, a sufficient quantity of water (30 c.c.) was added. The crystalline precipitate was collected and well washed with

dilute acetic acid. It was recrystallized from dilute acetone, colourless needles, m.p. 195–195.5°. (Yield 0.8 g., 70% of the theoretical. Found: N, 4.56. Calc. for $C_{14}H_{10}O_2NBr$: N, 4.60%.)

(iii) *3-Bromo-2-aminodiphenylene oxide.* 3-Bromo-2-acetaminodiphenylene oxide was boiled with alcoholic potash (2%, 50 c.c.) for one hour, and sufficient water (100 c.c.) was added to the solution, when a white crystalline precipitate was formed. It was recrystallized from dilute alcohol, colourless plates, m.p. 129–130°. (Yield almost theoretical. Found: N, 5.30. Calc. for $C_{12}H_8ONBr$: N, 5.34%.)

(iv) *3-Bromo-2-hydroxydiphenylene oxide.* 3-Bromo-2-aminodiphenylene oxide (0.15 g.) was heated in 10% sulphuric acid (15 c.c.) to obtain its sulphate. The sulphate was diazotized with sodium nitrite (0.05 g.) at 0°. On keeping the reaction mixture over night at 0°, the diazo-compound separated in a yellow crystalline precipitate. It was dissolved in a minimum quantity of water and the solution was added to a 50% solution of copper sulphate (40 g.), the latter being distilled during the addition so as to keep the concentration of copper sulphate constant.[12] After all the diazotized solution was added, the distillation was continued under the addition of water until no more crystals distilled. The crystalline substance was recrystallized from dilute alcohol, colourless needles melting at 113–113.5°. No depression was observed in the mixed melting point of this substance and the bromo-2-hydroxydiphenylene oxide obtained by the direct bromination of 2-hydroxydiphenylene oxide.[2]

(4) **3-Bromodiphenylene oxide.** 3-Bromo-2-aminodiphenylene oxide (0.1 g.) was converted into its hydrochloride by heating with 10% hydrochloric acid (15 c.c.). The hydrochloride was diazotized with sodium nitrite (0.035 g.). After three hours, this solution was made alkaline with caustic soda solution, filtered from reddish brown precipitate, and poured into sodium stannite solution made from stannous chloride (0.1 g.) and an excess of caustic soda solution. Nitrogen was evolved and a white crystalline precipitate separated. After being allowed to stand over night at room temperature, the precipitate was collected and recrystallized from dilute alcohol. It crystallized in colourless plates melting at 107–108°, and gave no depression of the melting point when mixed with 3-bromodiphenylene oxide prepared from diphenylene oxide by direct bromination in carbon disulphide.[13]

(5) **2,3-Dibromodiphenylene oxide from 3-bromo-2-aminodiphenylene oxide.** 3-Bromo-2-aminodiphenylene oxide (0.15 g.) was heated in hy-

(12) D. R. P., 167211.
(13) F. Mayer and W. Krieger, loc. cit.

drobromic acid (1.5 c.c. of an acid with density 1.38 diluted to 10 c.c.). The hydrobromide thus obtained was diazotized at 0° with sodium nitrite solution. After being kept over night at 0°, it was filtered from some reddish brown precipitate and was poured into cuprous bromide solution (0.2 g. cuprous bromide dissolved in 4 c.c. of hydrobromic acid with density 1.38 and diluted to 10 c.c.), when nitrogen was evolved and some yellow precipitate was obtained. It was recrystallized from 50% alcohol, when it separated out in plates melting at 150–150.5° (Yield 0.02 g.).

(6) **2,3-Dibromodiphenylene oxide from 3-nitro-2-aminodiphenylene oxide.** 3-Nitro-2-aminodiphenylene oxide was obtained from 2-acetaminodiphenylene oxide in a manner just as described by the previous authors.[14]

(i) *3-Nitro-2-bromodiphenylene oxide.* As the basicity of 3-nitro-2-aminodiphenylene oxide is extremely weak and neither its sulphate nor its hydrochloride is stable in water, the diazotation of this compound was carried out by a special method.[15] Sodium nitrite (0.026 g.) was dissolved in well cooled concentrated sulphuric acid (18 c.c.) and to it fine powder of 3-nitro-2-aminodiphenylene oxide was added at 0°. A small quantity of ice (8 g.) was added bit by bit into this solution and after being kept at 0° for one hour, it was poured on ice (70 g.). This diazo-solution was added to a solution of cuprous bromide in hydrobromic acid (1 g. of cuprous bromide dissolved in 18 c.c. of hydrobromic acid with density 1.38 and diluted to 50 c.c. with water), when nitrogen was evolved and a yellow crystalline precipitate separated out. After being allowed to stand over night, it was collected and recrystallized from alcohol, yellow needles melting at 171–172°. (Yield 0.4 g. Found: N, 5.05. Calc. for $C_{12}H_6O_3NBr$: N, 4.79%.)

(ii) *3-Amino-2-bromodiphenylene oxide.* 3-Nitro-2-bromodiphenylene oxide (0.38 g.) was dissolved in a solution of stannous chloride in glacial acetic acid saturated with hydrogen chloride, and after being allowed to stand over night at room temperature, this solution was heated on a water bath for half an hour. By adding an excess of caustic soda solution, the amino-compound was obtained in fine crystals. It was purified by recrystallization from dilute alcohol when it separated out in colourless needles melting at 172–172.5°. (Yield 0.2 g. Found: N, 5.43. Calc. for $C_{12}H_8ONBr$: N, 5.34%.)

(iii) *2,3-Dibromodiphenylene oxide.* 3-Amino-2-bromodiphenylene oxide (0.15 g.) was converted into its sulphate by heating with 10% sulphuric acid (30 c.c.) and the sulphate solution was diazotized with sodium nitrite (0.05 g.). After being allowed to stand over night, the diazo-solution was

(14) W. Borsche and B. Schacke, loc. cit.
(15) E. Misslin, *Helvetica Chim. Acta*, **3** (1910), 626.

filtered from reddish brown precipitate and poured into a solution of cuprous bromide in hydrobromic acid (0.2 g. of cuprous bromide dissolved in 5 c.c. of hydrobromic acid with density 1.38 and diluted to 15 c.c. with water), when nitrogen was evolved and an orange yellow precipitate separated out. After two hours this was collected and recrystallized from dilute alcohol, colourless plates, m.p. 150.5–151°. No depression was observed in the mixed melting point of this substance and 2,3-dibromodiphenylene oxide obtained from 3-bromo-2-aminodiphenylene oxide (5).

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THE CONCENTRATION OF DEUTERIUM IN SOME INDUSTRIAL WATERS.

By Masao HARADA and Toshizo TITANI.

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As the water from commercial electrolytic cells containing a little more deuterium than ordinary water is regarded as a convenient material for the preparation of heavy water, it seems worth while to examine the waters of other industrial sources on their deuterium contents. Thus, Newell and Ficklen[1] found that the water from some commercial chromium plating baths which had been operated for less than three years was heavier than ordinary water by 20 to 640 parts per million (p.p.m.); Washburn and Smith[2] also examined the same sort of water but found that the excess in density was only 2 to 5 p.p.m.; Uhlmann[3] called attention to the fact that the water from some laboratory storage batteries after six to ten years use was heavier than normal water by 33 p.p.m., suggesting that this water can be used as a starting material for the preparation of heavy water.

The present authors have also investigated some of the industrial waters on their deuterium contents by comparing their densities with that of normal water. The results are shown in the Table.

(1) L. L. Newell and J. B. Ficklen, *J. Am. Chem. Soc.*, **55** (1933), 2167.
(2) E. W. Washburn and E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305.
(3) W. Uhlmann, *Naturwissenschaften*, **22** (1934), 119.

Source of sample.	Period of operation	Readings in bouyancy balance.	Excess in density in p.p.m.	$H^2 : H^1$
(1) Commercial electrolytic cell	1 year	$0.39° \pm 0.00$	28	1 : 2100
(2) Chromium plating bath	4 years	$0.12° \pm 0.00$	7	1 : 3800
(3) Lead accumulator A.	9 years	$0.01° \pm 0.01$	3	1 : 4400
,, ,, B.	,, ,,	$0.00° \pm 0.01$	0	1 : 5000
,, ,, C.	,, ,,	$0.00° \pm 0.02$	0	1 : 5000
(4) Edison battery A.	9 months	$0.41° \pm 0.02$	28	1 : 2100
,, ,, B.	6 months	$0.38° \pm 0.02$	27	1 : 2100

The first sample to be investigated was the water from a commercial electrolytic cell, which, having been in use for all the year round, had been supplied with water sixty times its volume mainly owing to evaporation. The second sample was obtained from a commercial chromium plating bath running for nearly four years. During the process of plating, the evolution of hydrogen was hardly avoidable. The third samples were obtained from three different lead accumulators, all of which, having run for nearly nine years, had a supply of considerable amounts of water for the loss of the contents. The fourth samples were obtained from two Edison batteries, one being in use for about nine months in a part of coal mines, and the other for six months in another part of coal mines.

Various samples of water thus obtained were purified by the following processes: The water was filtered and distilled, after being neutralized if necessary, to free it from any dissolved substances; it was again distilled after being boiled with potassium permanganate in alkaline solution for nearly eight hours; then the distillate was redistilled twice, once with a few drops of sulphuric acid and once with some solid baryta. The water thus obtained was further subjected to three more successive distillations in the stream of air free from carbon dioxide, the first distillation being carried out under the addition of potassium permanganate and a few drops of sulphuric acid, the second under the addition of some solid baryta, and the final with a quartz condenser. The purity of the final distillate was determined by the conductivity method.

The density of the purified sample was determined referring to that of the ordinary water purified in the same way as above by the method of bouyancy balance using a quartz sinker. In order to increase the sensitivity of the balance, temperature a little lower than that of the room was employ-

ed, namely between 8° and 9°C., except the case (3) A, where the bath temperature was 23.80°C. The third column of the table shows the readings in the bouyancy balance in terms of degree, each being the mean of two independent determinations, except the case (3) A, where the mean of three independent determinations was taken.

If it is assumed that the increase in density is solely due to the enrichment of deuterium, the water from the commercial electrolytic cell contains about twice as much deuterium as ordinary water, which is almost the same for the cells which have been used for a longer period.[4] Therefore, the water in the electrolytic cell seems to be capable of being concentrated up to this value, after which the rate of concentration becomes much slower. The present result for the chromium plating bath agrees fairly well with that of Washburn and Smith, but not with that of Newell and Ficklen. The result for the lead accumulators is found to be not in argeement with that of Uhlmann who found as much increase in density as 32 p.p.m. The degree of concentration for this case may be largely affected by the process of charging, as the evolution of hydrogen gas during this process can be regarded as the main cause of concentration. It seems rather plausible that our result for the lead accumulators is related in some way to the relatively poor separation efficiency obtained when dilute sulphuric acid solution is electrolysed between lead electrodes.[5]

The result for the Edison batteries is quite unexpected. The samples were taken from quite different sources and they were purified in the same way as the other samples. We are not yet sure whether the increase in density is really due to the concentration of deuterium or to some unseparable impurities included originally. We are still in the course of re-investigation of this case.

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(4) D. H. Rank, *J. Chem. Phys.*, **1** (1933), 750.
(5) T. Titani, K. Kurano, and M. Harada, this Bulletin, **9** (1934), 269.

ON THE CONTENT OF DEUTERIUM IN THE WATER OF CRYSTALLIZATION.

By K. OKABE, M. HARADA, and T. TITANI.

Received August 28th, 1934. Published October 28th, 1934.

It has been reported by Güntherschulze and Keller[1] that no concentration of deuterium occurs when the volume of a given amount of water is contracted by repeating the process of dissolving and crystallizing Na_2SO_4 in it. We have also examined the same process. Although the result has been negative, it may be worth while to state our method in some details, since it has been found by several investigators that the water crystallized in some native minerals was heavier than normal water.[2][3]

About 20 liters of tap water was saturated with Na_2SO_4 by dissolving the anhydrous salt in it. The solution was then quickly cooled down by dipping the containers in ice water. The deca-hydrate which crystallized out, after being separated from the mother liquor (R_1), was heated in a beaker to convert it into anhydrous salt, and the remaining clear solution (C_1) was then filtered. Both C_1 and R_1, equal in volume, were subjected to the same process as mentioned above. A part of water (C_2) crystallized out from C_1 and the residual water (R_2) from R_1 were subjected to the third process, all the other water being discarded. The same process was repeated eight times until we obtained finally about 100 c.c. of water of crystallization and about an equal amount of residual water. The densities of these two parts of water, after being carefully purified, were compared with that of normal water by a quartz bouyancy balance. Both were found heavier than normal water by 2 parts per million, but no difference in density between themselves was found within one part per million, showing that no concentration occurred in this process. The same process carried out with Na_2CO_3 by Mr. Gotoh in our laboratory brought about the same result.

We may draw a conclusion that no isotopic fractionation occurs by the crystallization of water with such salts as above at least at low concentrations of deuterium and that the concentration of deuterium which were found in some of the native minerals might be due to the crystallizing out

(1) A. Güntherschulze and F. Keller, *Z. Elektrochem.*, **40** (1934), 182.
(2) E. W. Washburn and E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305.
(3) Peters, *Z. Elektrochem.*, **40** (1934), 474.

of the water that had been already concentrated in some way, presumably by a slow evaporation in a closed basin, as already pointed out by Washburn and Smith.[2]

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THE COLLOIDAL BEHAVIOUR OF SERICIN. VI.*

By Hideo KANEKO.

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Part II.

COLLOIDAL BEHAVIOUR OF SERICIN A AND SERICIN B.

Sec. I. The Solubility of Sericin A and Sericin B.

Sericin A and sericin B, obtained by the fractional precipitation from the sericin solution with ammonium sulphate, differ in many properties from the natural sericin existing on the cocoon fibers. At the ordinary temperature the precipitation is accompanied by slight chemical change and is irreversible. Precipitated sericins are only very slightly soluble in cold water, and their solubilities and degrees of dispersion increase remarkably on both sides of the isoelectric point and also in dilute salt solutions. While sericin B is white, sericin A has a slightly gray colour. The solubility of sericin A is diminished more easily by heat or by the action of air than that of sericin B.

(1) **Solubility of the Precipitated Sericins in Alkalis and Acids.** The chemical constitution of the sericin molecule decides the general properties of sericin. The most active groups in the molecule are the basic amino-group and the acid carboxyl-group. So hydrogen- and hydroxyl-ions have a

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* Continued from p. 421 of this volume.

predominating influence both on the solubility of sericin in water and on the physico-chemical properties of its solution. The solubility of proteins depends generally on the quantity present. Such an anomalous solubility of sericin was investigated by K. Kondo, and I also noticed it with sericin A and sericin B. The definite quantities of sericin A or B were taken in small conical flasks containing 100 c.c. of 0.005 mol NaOH solution, and the flasks were frequently shaken and left in a thermostat of 14°C. for 48 hours. The nitrogen contents of the solutions were determined after treating them by a centrifuge.

The solubility of precipitated sericins in dilute alkali solutions increases first with increasing quantity of sericin, reaching a maximum point, and then diminishing gradually. Sericin A is less soluble in alkali than sericin B.

(a) **Effect of *p*H on Solubility.** Fairbrother and Swann[53] showed that, with increasing concentration of either acid or alkali, more and more gelatin goes into solution, that acid or alkali disappears from the solution, and that there is a definite minimum point of solubility in very dilute acid.

(i) **Solubility in Alkali.** The precipitated sericin (1 g.) was put in 100 c.c. of alkali solutions having various hydrogen-ion concentrations under the same conditions described above, and the quantity of dissolved nitrogen was determined by Kjeldahl method and *p*H value of the solutions by the electrical method, (Table 91).

Table 91.

Solubility of Sericins in NaOH Solution at 20°C.

Original NaOH solution *p*H	Sericin A		Sericin B	
	*p*H (2 days after)	Dissolved quantity (%)	*p*H (2 days after)	Dissolved quantity (%)
5.7	6.7	7.96	6.7	9.95
7.2	6.8	8.18	6.8	10.17
11.0	7.4	9.75	7.2	11.15
12.0	8.5	12.38	8.4	12.82

As observed by Fairbrother and Swann, the solubility (g./100 c.c.) of sericin A or sericin B in the alkali solution increases with increasing concentration of alkali and at the same time alkali disappears from the solution, that is, the *p*H value diminishes by the addition of sericin.

The precipitated sericins were found slightly more soluble in KOH solution than in NaOH solution.

(53) Fairbrother and Swann, *J. Chem. Soc.*, **121** (1922), 1237.

(ii) **Solubility in Acid.** Under the same conditions described above, I determined the solubilities of the precipitated sericins in acid solutions having various hydrogen-ion concentrations, (Table 92).

Table 92. Solubility of Sericins in HCl Solution.

Original HCl solution *p*H	Sericin A			Sericin B		
	*p*H (2 days after)	Dissolved quantity (%)	*V*	*p*H (2 days after)	Dissolved quantity (%)	*V*
3.8	6.4	7.74	2.8	6.3	9.51	4.0
3.4	6.0	7.07	2.6	5.9	8.85	3.4
3.0	5.4	6.25	2.0	5.3	7.60	2.9
2.75	4.7	5.75	1.9	4.7	7.32	2.7
2.4	4.6	5.67	1.7	4.6	7.35	2.7

V: the quantity (c.c.) of 0.1 N HCl combined with sericins.

The existence of a well-marked point of minimum solubility over a narrow range of hydrogen-ion concentration is characteristic of most proteins, and the point of minimum solubility is *p*H 4.5 for sericin A and *p*H 4.7 for sericin B, as shown in Fig. 39.

On account of slight denaturation on precipitating sericins, their isoelectric points are displaced to the more alkaline side than that of natural sericin.

The point of minimum solubility in sulphuric acid solution was found *p*H 4.4 for sericin A and *p*H 4.6 for sericin B.

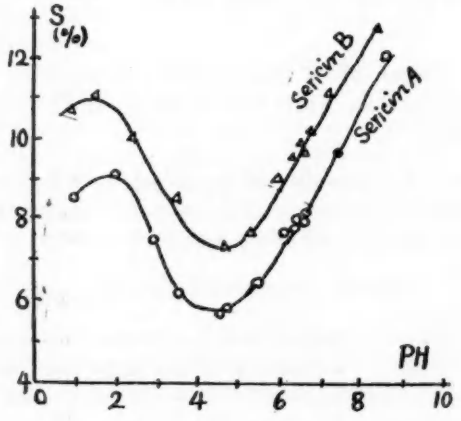

Fig. 39.

The results are summarized as follows:

(*a*) When precipitated sericins are added to the acid or alkali solution, acid or alkali disappears from the solution, sericin combining stoichiometrically with it.[54]

(54) J. Errera, *Compt. rend.*, **193** (1931), 1347.

(*b*) The solubility of sericin precipitated with $(NH_4)_2SO_4$ increases with increasing concentration of acid or alkali, reaching a maximum point, and then falling gradually.

(*c*) The precipitated sericins possess a minimum solubility near *p*H 4.5, which corresponds to the isoelectric point of natural sericin.

(*d*) The solubility of sericin A in dilute acid or alkali solution is less than that of sericin B.

(*e*) Both sericin A and sericin B are more soluble in HCl solution than in H_2SO_4 solution.

(b) **Effect of the Temperature on the Solubility.** The solubility of sericins depend on the hydrogen-ion concentration and also on the temperature as it is well known. The effect of the temperature on the solubility of sericins in HCl solution having *p*H 2.4 is shown in Table 93, where constant K was obtained by calculation from the formula $\log S - \log A = K \log t$ or $S = At^K$, S being the solubility of sericins, t the temperature, and A constant.

Table 93.

	Below 30°C.		Above 30°C.	
	K	$\log A$	K	$\log A$
Sericin A	0.027	0.685	0.024	−2.00
Sericin B	1.73	0.740	1.54	−1.55

Near 30°C. the variation in solubility of the precipitated sericins is remarkable, while the solubility of the natural sericin varies rapidly near 60°C.

(c) **Solubility in the Solutions of Sodium Salts of Organic Acids.** The precipitated sericin (1 g.) was introduced into 100 c.c. of 0.01 mol salt solution, and the solubility was determined at 20°C. after 48 hours (Table 94.).

Table 94.

Salt	Sericin A	Sericin B	Salt	Sericin A	Sericin B
HCO_2Na	10.01%	10.65%	$C_3H_7CO_2Na$	10.20%	9.51%
CH_3CO_2Na	9.98	10.01	$C_4H_9CO_2Na$	10.50	9.06
$C_2H_5CO_2Na$	10.01	9.73	$C_{17}H_{33}CO_2Na$	17.91	15.26

With increasing number of carbon atoms in the molecule of the salts, the solubility of sericin A increases slightly, while that of sericin B dimi-

nishes as is the case with the natural sericin and gelatin. In the solution of salts of higher fatty acids, such as oleate, sericin dissolves considerably as it is well known.

(2) **Buffer Capacity of Sericin A and Sericin B.** One gram of sericin A or sericin B was dissolved in a solution containing 1 milli-mol NaOH and the resulting solution was made up to 1 liter. Twenty c.c. of this solution were mixed with x c.c. of 0.01 N HCl and $(30-x)$ c.c. of distilled water. pH was determined colorimetrically when there was no interference by colour reactions, and by the quinhydrone electrode, when there was such.

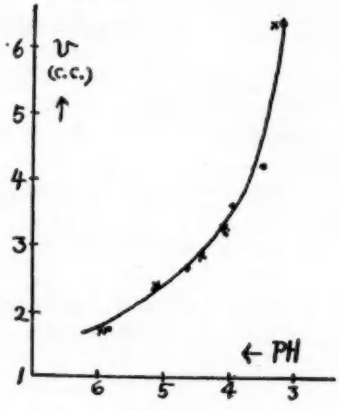

Fig. 40.

The buffer capacity of precipitated sericins is approximately equal to that of gelatin, and sericin A and sericin B have nearly the same buffer capacity as shown in Fig. 40, where dots are the values for sericin A (sericin B shows nearly the same values), crosses those for gelatin, and v denotes the number of c.c. of 0.01 N HCl added to 20 c.c. of the sericin solution. This fact leads to the conclusion that the isoelectric point of sericin A is near that of sericin B. In fact, the isoelectric points of sericin A and sericin B were found respectively pH 4.1 and pH 4.2 by comparing the degree of turbidity of their solutions.

Sec. II. The Electric Cataphoresis of Precipitated Sericins.

The isoelectric point of a protein must be the point at which an equal mumber of diffusible anions and cations are present owing to the dissociation of the protein complex, and under this condition the protein presents the amphoteric ion $R\begin{matrix}NH_3^+\\COO'\end{matrix}$. In acid solutions the ionization of the carboxyl-group is suppressed while the ionization of the ammonium-group is increased. The protein becomes then positive complex ion. In alkali solution or in solutions having a higher pH than that of the isoelectric point, the ionization of the ammonium-group is suppressed while the ionization of the carboxyl-group is increased. The protein is, then, electronegative.

One gram of sericin A or sericin B was dissolved in a solution containing 1 milli-mol NaOH and the solution was treated in the same manner as described before. The cataphoresis measurements were made by the microscopic method as shown previously. The results are shown in Tables 95, 96 and Fig. 41.

Table 95.

Cataphoretic Velocity of Sericin A.

Vol. of $\frac{N}{10}$ HCl added (c.c.)	*p*H		*U*(μ/sec. per 1 volt/cm.)	ζ(m.v.)
1.3	4.7	slightly milky	−0.701	−1.708
1.4	4.5	milky, ppt. later	−0.565	−1.376
1.5	4.35	,, ,,	—	—
1.6	4.2	,, ,,	−0.306	−0.743
1.7	4.05	most ppt.	—	—
1.8	3.95	ppt.	+0.306	+0.748
1.9	3.78	,,	—	—
2.0	3.7	milky, ppt. later	+0.391	+0.952
2.1	3.6	slightly milky	—	—

Table 96.

Cataphoretic Velocity of Sericin B.

Vol. of $\frac{N}{10}$ HCl added (c.c.)	*p*H		*U*(μ/sec. per 1 volt/cm.)	ζ(m.v.)
1.3	4.7	very slightly milky	−0.896	−2.163
1.4	4.5	milky, ppt. later	−0.767	−1.844
1.5	—	ppt.	—	—
1.6	4.25	most ppt.	0.00	0.00
1.7	—	ppt.	—	—
1.8	4.05	slightly milky	+0.283	+0.683
1.9	3.7	very slightly milky	—	—
2.0	3.6	,, ,, ,,	—	—

The electromotive potential developed on the interface between a protein particle and water may vary with *p*H of the solution. The charged protein particles can be precipitated from solution under such conditions as reduce the potential to less than 1.5 milli-volts. This reduction can be brought about by dilute solutions of salts, the active precipitating ion being the one carrying the opposite charge to the protein ion, and the effect being proportional to the valency of the ion as already shown. Debye and Hückel's formula indicates that, for a given potential difference E, there is a direct proportionality between the potential of the double layer and the cataphoretic velocity, U (μ/sec.) :

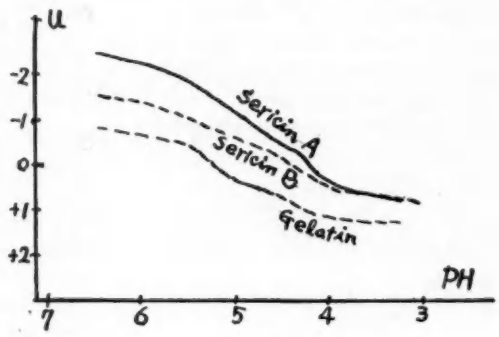

Fig. 41.

$$\zeta = \frac{6\pi\eta U}{ED} .$$

From Table 94 and 95 it can be found that the isoelectric points of sericin A and sericin B in very dilute alkaline solutions exist respectively near *p*H 4.1 and *p*H 4.25, and that the rate of migration of sericin A is slightly greater than that of sericin B.

The flattened form of the sericin curves in Fig. 41 indicates that sericin remains electrokinetically very sluggish over the whole range. This leads us to the suspicion that sericin, like gelatin, is less reactive both as an acid and as a base than egg albumin. M. Samec[55] showed that amylopectin possesses a greater cataphoretic velocity than any other component of starch though it is the most hydrated.

Effect of Salts. The cataphoretic velocity of sericin is influenced by the presence of salts as well as by *p*H (Table 97).

The influence of salts on the surface potential of sericin A is shown in Fig. 42. Small quantities of an electrolyte having a monovalent cation raises the boundary charge. Since this increase is due to the negative ion,

(55) M. Samec, *Kolloid-Beihefte*, **33** (1931), 269–278.

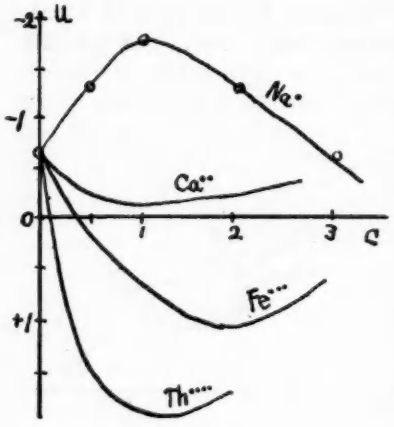

Fig. 42.

Table 97.

Salt	Sericin A		Sericin B	
	U(μ/sec.)	ζ(m.v.)	U(μ/sec.)	ζ(m.v.)
NaCl	−1.797	−4.501	−1.972	−4.873
KCl	−2.01	−5.032	−2.386	−5.895
$CaCl_2$	−0.122	−0.306	−0.487	−1.203
$MgCl_2$	−0.378	−0.946	−0.235	−0.5806
$AlCl_3$	+0.590	+1.470	+0.127	+0.3119
$FeCl_3$	+0.500	+1.245	+0.368	+0.906
$Th(NO_3)_4$	+2.010	+5.032	—	—

The concentration of the salt solutions is 0.001 mol and the volume added is 1.0 c.c.

the influence of the latter in minute concentration seems to exceed the discharging effect of a monovalent cation. In the case of a divalent or trivalent cation, however, the discharging effect of that ion comes immediately into force.

Sec. III. Some Properties of Sericin A and Sericin B.

(1) The Gold Number. The gold numbers of sericin A and sericin B in N/3000 NaOH solution are given in Table 98.

Table 98.

Conc. (%)	Sericin A	Sericin B
0.10	0.025	0.035
0.16	0.023	0.0295
0.22	0.0185	0.021
0.30	9.014	0.018

The protective action of sericin A is greater than that of sericin B under the same conditions.

(2) The Apparent Specific Gravity. It is known that in most hygroscopic materials a contraction in total volume occurs during adsorption of water, and this is probably true for sorption in general. When such occurs, an *apparent* density will be obtained which is greater than the *true* density.

Sericin A and sericin B swell in various solutions and liquids. The specific gravity of sericin measured by the usual submersion method will, therefore, vary with the liquids used. So the true specific gravity cannot be obtained, but the apparent one depending on the nature of the liquid.

Table 99.

App. density	Liquid used	Author
1.361	Hot water	Müller
1.350	Cold water	J. Kubota[56]
1.33	Benzine	—

Further, from the value of the apparent density we can presume the order of swelling of sericin in liquids. In an active solvent in which sericin swells, the apparent specific gravity is greater than in an inactive solvent. This fact can be seen for the apparent density of raw silk (Table 99).

The apparent density of raw silk depends on the quantity of sericin remaining on the silk fiber, and on the liquid used. The apparent density of sericin A and sericin B is shown in Table 100.

Table 100.

Apparent Specific Gravity of Sericins (15°C.)

Liquid used	Sp. gr. of liquid (15°C)	Sp. gr. of sericin A	Sp. gr. of sericin B	Diff.
Acetone (1)	0.8071	1.412	1.339	0.073
,, (2)	0.7989	1.404	1.322	0.082
C_2H_5OH	0.7955	1.3947	1.3690	0.0257
HCOOH	1.1640	1.374	1.357	0.017
Pyridine	1.0004	1.370	1.353	0.017
CH_3COOH	1.0713	1.370	1.368	0.002
$C_6H_5NO_2$	1.0209	1.3688	1.328	0.0408
CH_3OH	0.8019	1.366	1.353	0.013
C_6H_6	0.8848	1.375	1.344	0.013
Water	1.000	1.356	1.309	0.047
$C_6H_4(CH_3)_2$	0.8642	1.283	1.265	0.018

(1) Merck's acetone.

The active solvents in which precipitated sericin swells are acetone, ethyl alcohol, formic acid, and pyridine. Benzene and xylene which have no or small permanent dipole moment are inactive.

Nitrobenzene, methyl alcohol, and acetic acid are moderately active solvents for sericin. It was impossible to determine the true density of the powdered sericin.

The reciprocal values of densities of proteins are shown in Table 101.

(56) J. Kubota, *Bull. Sericul. and Silk Ind. Japan*, **5** (1932), 68–69.

Table 101.

Protein	$1/d$	Protein	$1/d$
Sericin A	0.736 (in benzene)	Gelatin	0.724
Sericin B	0.744 (,, ,,)	Egg-albumin	0.735
Fibroin	0.740 (in water)	Serum albumin	0.735

(3) Colour Reactions of Sericin A and Sericin B.

Table 102.

Solution of Precipited sericins in N/10 NaOH.

Colour reaction	Sericin A	Sericin B
Engel's reaction	none	none
Million's reaction	given	given (deeper red)
Arginine reaction	given (5.95%)*	given (3.50%)*
May and Rose's and Neubauer Rhode's reaction	given faintly	none
Sulphur reaction	given faintly	given faintly
Histidin reaction	given	given
Biuret reaction	violetish red	violetish red
Xanthoprotein reaction	given	given

* By colorimetry.

Recently the existence of tryptophane in sericin has been reported by Abderhalden.[57]

The Biuret Reaction of Sericin A and Sericin B. The red tinge of the biuret colour reaction of sericin sol has qualitatively an intimate relation with the quantity of sericin in it, but the colour is influenced by the presence of other substances in the cocoon layer. So it was impossible to determine quantitatively the degree of "kaijo" of cocoons by the colour of the biuret reaction of sericin sol.

(57) Abderhalden, *Z. physiol. Chem.*, **202** (1931), 37, ibid., **207** (1932), 141-146.

(4) Fluorescent Colours of Sericin A and Sericin B Solutions under the Ultraviolet Light. When the sericin A and sericin B solutions in dilute alkali are exposed to the ultraviolet light, both give a slight yellow fluorescence. If a minute amount of glycocoll which is contained in the solution of the natural sericin and gives slight violet fluorescence be added to the sericin solutions, there is no variation in fluorescent colour of the sericin A solution, while the sericin B solution gives immediately a brilliant violet fluorescence. If the sericin A and sericin B solutions contain small amounts of aspartic acid, both give the same violet fluorescence. The fluorescent colours produced by the sericin solutions are influenced by the presence of a minute quantity of salts. From these results it can be seen that the fluorescent colours depend on the impurities adsorped or occluded in the cocoon layers which have close relation with the variety of cocoons, and on the proportion of sericin A and sericin B which is also intimately related to the variety.

(5) Transformation from Sericin A to Sericin B. Sericin A is more sensitive to heat than sericin B. So sericin A is transformed gradually into sericin B by heating it in drying apparatus, by steaming or by heating its solution in a flask.

Sec. IV. The Swelling of the Sericin A and Sericin B.

It will be interesting to note that substances like gelatin, casein, sericin, and starch, which are proved to be amorphous by X-ray analysis of Debye and Scherrer are the very substances that show the phenomenon of swelling. But the stretched sericin A will be shown to be crystalline by X-ray examination as done in the case of fibroin.

Sericin, when dry, is hygroscopic and it contains usually about 10% water. The sericin immersed in water gradually swells, or imbibes water. The swelling of the precipitated sericin in water and in the solutions of acids was investigated by M. Oku,[58] who showed that the swelling of the precipitated sericin in very dilute acid solutions possesses a minimum point in 1/1024 mol HCl or H_2SO_4 solution, and that it swells more in HCl solution than in H_2SO_4 solution.

The swelling of proteins belongs to complex phenomena and it depends on the expansion of colloidal micellæ, and on the adsorption and imbibition of liquid molecules or ions. This phenomenon of swelling has naturally a close relation to the "kaijo" of cocoons. Precipitated sericin (0.2 g.) was

(58) M. Oku, *Reports Gunze Phys. Chem. Lab. Japan*, 4 (1929), 15–22.

put in centrifuge tubes with scales, mixed with 10 c.c. of water or a salt solution, and then left to stand for 24 hours at 20°C. After the equilibrium was reached it was treated in a centrifuge for 30 minutes and the increase in volume of the sericin referred to the original was taken as expressing the comparative degree of the swelling.

(1) The Swelling of Sericins in the Solutions of Organic Sodium Salts. **(a) Sericin A.** I used the sodium salts, for their anions are the least surface capillary active (Table 103 and Fig. 43).

Table 103.

	C_m	O
HCO_2Na	0.50	0.73
CH_3CO_2Na	0.33	2.84
$C_2H_5CO_2Na$	0.25	8.93
$n\text{-}C_3H_7CO_2Na$	0.21	19.6
$n\text{-}C_4H_9CO_2Na$	0.125	68.5

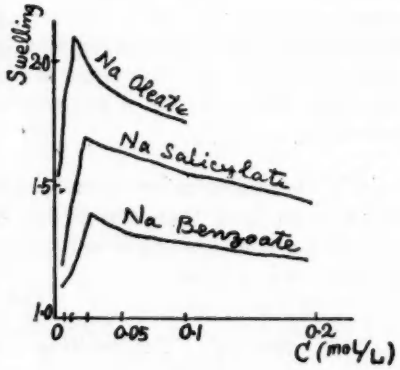

Fig. 43.

In the sodium salt solutions of fatty acids the concentration for the minimum swelling of sericin A, C_m, decreases with increasing number of carbon atoms in their molecules and it has the following relation with capillary activity of the fatty acids, O,

$$\log O = 3.0 - 8.2\, C_m .$$

The maximum swelling in the solution of oxalate or salt of an oxy-acid is coincident with the minimum point in the solutions of sodium salts of fatty acids, and at the concentration of 2 mol and in concentrations less than 0.125 mol the arrangement of the anions according to the type and the intensity of their influence on swelling leads to the Hofmeister series: citrate $<$ tartrate $<$ acetate. As the precipitated sericin adsorbs strongly the anion of sodium oleate, it has a maximum point of swelling in very low concentration of the salt (0.012 mol).

The relation between the concentration of the minimum swelling of sericin B and the number of carbon atoms of the salts of fatty acids was

contrary to the case of sericin A. The results were similar to those of their solubilities in the solutions of the same salts.

Taking the swelling of the precipitated sericin in distilled water at 20°C. as 100, the effects of salts on swelling are shown in Table 104.

Table 104. (Sericin A).

Mol	2	1	0.5	0.25	0.125	0.0625	0.0312
HCO_2Na	122.5	98.4	77.4	85.5	87.1	93.5	
CH_3CO_2Na	114.5	98.4	83.8	80.6	101.6	109.6	—
$C_2H_5CO_2Na$	150.0	132.2	104.8	98.6	109.6	130.6	—
n-$C_3H_7CO_2Na$	117.7	116.1	112.9	108.0	111.2	114.5	—
n-$C_4H_9CO_2Na$	—	145.1	119.3	112.9	101.6	106.4	109.6

The numbers less than 100 mean contraction in the solutions. In general sericin B swells more in the solutions of these salts than sericin A.

(2) Swelling in the Solutions of the Sodium Salts of Inorganic Acids. In the solutions of capillarily inactive sodium salts of inorganic acids sericin A and sericin B swell as well as in the solutions of capillarily active organic salts. But the concentration of the maximum swelling is greater than in the case of organic salts.

(3) Effect of Acids and Bases. The swelling of both sericins depends remarkably on the *p*H of the solutions as it is well known, and the minimum swelling of sericin A in HCl solutions corresponds to *p*H 3.75. Different acids causes different degrees of swelling.

Loeb (1922) considered that swelling was affected not only by the hydrogen-ion concentration, but also, in acid solutions, by the valency of the anion. Sericin A and sericin B swell considerably in a very dilute alkali solution and in concentrations higher than 1/40 mol NaOH the former disperses partly into solution.

The swelling of sericins in solutions of HCl and of NaOH is shown in Fig. 44. The acid curve rises sharply to the maximum at an external *p*H of 3.0; the alkaline curve rises slowly at first. The isoelectric point of sericin A exists on the more acid side than that of sericin B as frequently described.

(4) Effect of Temperature. The variation in swelling of sericins with rising temperature is shown in Fig. 45, where $\log S$ is given by the equa-

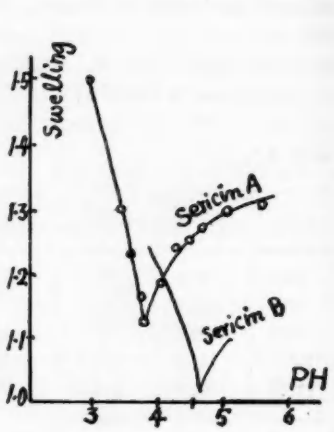

Fig. 44.

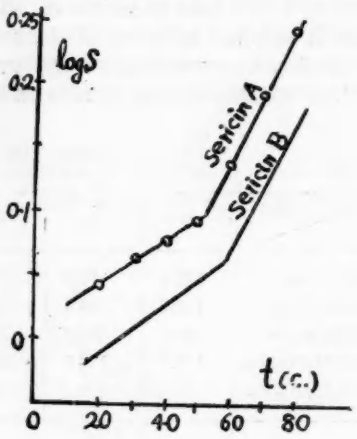

Fig. 45

tion : $\log S = A + Bt$ or $S = A'e^{Bt}$, where A and B are constants, the former depending on pH and on the state of sericin, and the latter on the state only. For example, $\log S = 1.33 + 0.005\,t$ (below 50°C.), and $\log S = 1.54 + 0.14\,(t-50)$ (above 50°C.) for sericin A at pH 4.6. The abrupt change at 50°C. caused by the rapid transformation of gel into sol can also be seen in other properties.

Lloyd[59] showed that the quantity of absorbed water in gelatin is proportional to the square of temperature at low temperatures. If the quantity of adsorbed water be proportional to the increase in volume of sericin, the swelling may be proportional to the square of temperature. Such relation can be found in the results of this experiment.

(To be continued.)

(59) Lloyd, *Biochem. J.*, **21** (1929), 21, 1352; ibid., **22** (1928), 1007; ibid., **24** (1930), 1460; ibid., **25** (1931), 1580.